

Appendix 2.4 B2

Task 2.4 B2: Denitrification of Reverse Osmosis Brine Concentrate by Anaerobic Fluidized Bed Biofilm Reactors with Granular Activated Carbon Media

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Preface

The Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable, and reliable energy services and products to the marketplace.

The PIER Program, managed by the California Energy Commission (Commission), annually awards up to \$62 million to conduct the most promising public interest energy research by partnering with Research, Development, and Demonstration (RD&D) organizations, including individuals, businesses, utilities, and public or private research institutions.

PIER funding efforts are focused on the following six RD&D program areas:

- Buildings End-Use Energy Efficiency
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- Renewable Energy
- Environmentally-Preferred Advanced Generation
- Energy-Related Environmental Research
- Strategic Energy Research.

What follows is the final report for Task 2.4 B1 of the Electrotechnology Applications for Potable Water Production and Protection of the Environment Contract Number 500-97-044.

Executive Summary

Introduction

Recycled water has become one of the significant resource used to replenish the existing water bodies, especially in the states where the production of sufficient water of high quality can not meet the demand of growing population. Among the technologies employed to obtain recycled water are membrane processes such as microfiltration, ultrafiltration, reverse osmosis. Recycled water passed through a reverse osmosis membrane is considered highly pure and safe for use.

Purpose

Similar to all other environmentally applicable techniques, the brine concentrates generated by reverse osmosis are, despite their small volumes, hazardous and must be handled properly in order to avoid significant environmental impact and abide by the environmental regulations. It is important to determine the disposal or treatment strategies for such brines ahead of time during the planning stage of a membrane purification plant, as it may become a problematic issue later.

Project Objectives

Fluidized Bed Biofilm Reactors charged with Granular Activated Carbon (FBBR-GAC) were chosen as a promising technology for the nitrification and denitrification of reverse osmosis brine concentrates to remove nitrates and sulfates. This research would also create a model to describe the process dynamics and implement inexpensive pilot-scale testing. Several batch experiments were conducted to find the optimum environmental parameters for the highest possible removal efficiency. Biokinetic parameters were obtained from continuous chemostat tests to best describe the conditions in the actual system. Additionally, a series of experiments were conducted to predict the denitrification efficiency of the FBBR-GAC column and to verify the model.

Project Outcomes

The FBBR-GAC system has proven very efficient both in terms of process and energy consumption for the denitrification and sulfate reduction of brine concentrates.

Conclusions

The optimum temperature and pH range for the denitrification was determined in this research. Other conclusions of this study included that the total dissolved solid (TDS) concentration had insignificant effect on the denitrification rate. Most importantly, preliminary laboratory-scale

experiments revealed that the FBBR-GAC process is capable of removing approximately 45% of sulfate and 100% nitrate.

Recommendations

It is recommended that the FBBR-GAC process be further investigated in laboratory scale as well as in pilot scale in order to assess its energy efficiency and cost-effectiveness. Sulfate reduction is an additional advantage of the FBBR-GAC system described above. However, more investigation is needed in order to upgrade the system for better sulfate removal.

Benefits to California

As the membrane process technology slowly replaces the conventional treatment technology in the water recycling practice in the State of California, it is anticipated that water reclamation facilities will greatly benefit from the treatment of brine concentrates. The process of reverse osmosis is advantageous in coastal areas. Due to its geographical size, all areas in California are not close to the ocean. This makes brine disposal challenging. The processes in the research address such problems and could alleviate and allow area far from the coast to take advantage of reverse osmosis.

Abstract

Reverse osmosis (RO) membrane process used in water recycling facilities is a viable and cost-effective alternative to the state-of-the-art treatment technologies. RO membranes produce a treatment by-product referred to as brine concentrate that must be handled properly prior to disposal. The high ammonia, salt, sulfate and heavy metal content of RO brines renders them hazardous to the environment when dumped untreated. As the RO membranes become widely used, the concentrated brines generated as the treatment by-products will be likely to become a serious obstacle in the application of this process due to possible promulgation of regulations regarding the MCL limits of the contaminants content.

This research employs a biological denitrification process known as fluidized bed biofilm reactor with granular activated carbon (FBBR-GAC) for the denitrification of RO brines. This process has been chosen because of its simplicity, efficiency, and cost-effectiveness in denitrification of waters and wastewaters. Due to the presence of biofilm, the FBBR-GAC process can support substantially more biomass than the conventional suspended growth biological processes. Additionally, the process affords trouble-free operation, lower capital and maintenance cost.

There are two main objectives to be achieved with this project. The first objective is to evaluate the feasibility of FBBR-GAC denitrification process for the brine concentrates. A series of bench-scale chemostat studies were conducted to determine the effects of influencing parameters such as temperature, pH, high TDS content and organic carbon source on the denitrification process.

The second objective is the application of a mathematical model for predicting the performance of FBBR-GAC denitrification process. The model simulation will be compared to the data obtained from the laboratory-scale FBBR-GAC system for calibration and verification purposes. Scale-up studies will be conducted to design the pilot and full-scale system by employing the techniques of dimensional analysis and similitude.

Key Words: Water recycling; brine; concentrate; reject; reverse osmosis; reverse osmosis concentrate; denitrification; fluidized bed; granular activated carbon; biofilm.

1. INTRODUCTION

1.1. Overall Review of Water Recycling

In the near future, it is likely that many nations will face serious water shortages due to pollution or limited water resources. Even with the available water sources that are of high quality as to provide potable water, the increase in population necessitates the production of sufficient water that can be safely used by millions of people. For example, California is among the states recently facing serious water shortages, which is expected to worsen unless some timely and preventive measures are adopted. It is estimated that by the year 2010, the net demand for water will be 35.6 million acre-feet with an annual deficit of about 2.3 million acre-feet, by which time, the state's population is anticipated to rise to 41 million (WateReuse Association, 1993; California State Water Resources Control Board, 1990). It is for this reason that water and wastewater districts in California have received early lessons on the importance of a well-organized and comprehensive approach to exploit other reliable water sources.

Water recycling is regarded as a new, reliable and economically viable alternative to the existing options including water conservation, desalination, import from other states, etc. Recycled water is defined in California Water Code as "the water, which, as a result of treatment of wastewater, is suitable for a direct beneficial use or a controlled use that would not otherwise occur" (EPA Guideline, 1992). Replacing the potable water used for non-potable purposes with some type of used water (where feasible) after treating it to the extent not to pose any health risks to the users, would preserve millions of acre-feet of water for potable use.

In recycling practices, municipal water is the source water that can be recovered through a series of treatment processes. After receiving treatment, the secondary effluent or a blend of primary and secondary effluent from the wastewater treatment plant is taken to the recycling plant. Here, it is provided with an advanced tertiary treatment so that the final effluent quality is high enough to be safely used by urban, agricultural and industrial water costumers for beneficial purposes.

The secondary effluent from the wastewater treatment plant requires further purification to ensure the compliance with the water quality standards. There is no EPA set standards for recycled water. The regulations in California are for unrestricted use only, i.e., recycled water is suitable for all applications except drinking (Myers, 1996). The basic principle underlying water

quality regulations pertaining to the recycled water is to assure that health protection is not compromised through its use. Where the human exposure is likely in a reuse application, regulations state that the recycled water should be treated to the highest degree possible prior to the reuse. It must be free of pathogens that could spread disease. Conversely, where public access to a reuse site can be restricted so that the exposure is unlikely, a lower level of treatment may be satisfactory. Direct reuse applications such as discharging the recycled water directly into the distribution system is prohibited by the regulations on the grounds that there are no real time microbiological quality assessment studies (EPA Guidelines, 1992). However, surface water augmentation and groundwater recharge are strongly encouraged since no negative health effects have been reported.

There are many advantages of water recycling, and its benefits to meet non-potable water demands are as follows:

- Many countries face rapid population growth. Therefore, water conservation efforts can only meet the present water needs. More effort needs to be directed towards conservation of potable water supplies. Water recycling is one of the best few alternatives that save the potable quality water sources.
- Some cities may lack water sources simply because of their location, or over-consumption of their existing water resources. Importing water is capital and energy intensive, politically tenuous and inconsistent from year to year. Instead, the existing limited sources could be augmented with recycled water, and this water could be used as a substitute for potable water for irrigation, industry, groundwater recharge, and surface water augmentation.
- For some inland cities, wastewater treatment costs could be high because of the need to protect the downstream water quality. At this point, water recycling proves to achieve downstream water quality criteria (Okun, 1991).
- Over-pumping of groundwater is a short-term and short-sighted solution to water shortage problems, as it may deplete groundwater basins. Recharging them with recycled water not only would keep the groundwater basin replenished, but also prevent salt water intrusion into groundwater aquifers.
- Seawater desalination has been practiced in many countries to obtain drinking water. However, it is an expensive potential water source with yet undefined environmental

constraints and considerations. Water recycling is proven to be more cost-effective than desalination in most cases.

- Recycling may well be a building block of economic growth in small communities with limited water supplies. It can provide reliable and affordable quantity of water that could be used for agricultural and industrial purposes. It may even attract new industries that would create new job opportunities for the community, and contribute to its development (Filteau, 1995).

In order to accomplish the high quality standards set by regulatory agencies for recycled water, water utilities are forced to use the best available technologies (BATs) in the market. Recently, much attention has been given to the membrane processes such as microfiltration, ultrafiltration and reverse osmosis. Among these, reverse osmosis (RO) is probably the oldest membrane technology, and has been in use to remove salts from brackish water and seawater for several decades. However, it has progressively developed into a more reliable unit operation that outperforms most conventional water treatment technologies. This membrane technology is considered to be a viable and economical option to convert the impaired sources such as pretreated wastewater into high quality water.

This research project is directed at developing a strategy for the removal of nitrates in the RO brine concentrate that employs anaerobic fluidized bed biofilm reactors with granular activated carbon (FBBR-GAC) for denitrification. As the membrane processes become widely used technologies in the water recycling practices, their by-products will likely to become a problem with respect to their treatment or disposal. With the upcoming water quality requirements, it is quite possible that the regulatory agencies would require proper pre-treatment prior to disposal of such brines. Therefore, it is necessary to include the best treatment option for the brine concentrates during the initial planning stage.

The feasibility and efficiency of FBBR-GAC technology will be assessed for RO brine concentrate with high nitrate, salt, sulfate and heavy metal concentrations. The effect of temperature, pH, salt and organic carbon on denitrification process will also be studied to optimize the performance and economy of anaerobic FBBR-GAC systems. A modeling and design protocol will be included to predict the process efficiency, and will be used as a design tool for process up-scaling.

1.2. Reverse Osmosis Brine Concentrate

1.2.1. Generation of Brine from Reverse Osmosis Membrane Processes and its Characteristics

Similar to most treatment technologies, membrane processes also produce wastes that require handling either by various disposal methods or by separate treatment processes. The waste product of RO process referred to as “brine” (brine reject or concentrate) is comprised of materials rejected by the membrane filter. RO systems can remove up to 97 percent of dissolved minerals, and more than 95 percent of most dissolved organics (Rorech and Bond, 1993). Reverse osmosis can achieve a total dissolved solids rejection in the range of 85-98 percent for all ions (Dietrich, 1995). The contaminants in the feed source are concentrated by a factor that is determined by the hydraulic ratios established by system design (Comb, 1994). It is regarded as a non-recyclable by-product of RO processes.

Contaminants that are initially in the feed water stream, and have not been removed by the membranes eventually end up in the system brine. The basic environmental concern with this waste stream is its more concentrated levels of contaminants due to the reduced volume. For example, if the RO recovery is 85 percent, 15 percent of the water or wastewater treated is discarded as brine concentrate. The increased waste concentration might be irrelevant and balanced out by the benefits of a reduced waste volume due to the fact that increased waste concentrations may pose hazards to the environment into which the brine is being discharged. Therefore, disposal of brine is one of the main factors influencing the feasibility of RO applications. Additionally, when a new technology is introduced to the market, its operational practicability and cost effectiveness must be established ahead of time not only for the technology itself but also for its side waste streams, so that it could be integrated into the initial planning. Determining the treatment alternative and testing the feasibility of the process for the side waste streams would avoid problems down the line with the regulatory agencies regarding their handling and disposal. An increase in environmental awareness and more stringent future regulations may restrict the disposal options. Therefore, new and promising treatment alternatives that are as functionally efficient and cost-effective as the traditional disposal methods should be introduced to the market.

The RO concentrate brines contain significant quantities of different contaminants, and therefore pose a threat to the environment. Literature is quite scarce in the area of the effects of

excess concentrations of common ions on living organisms other than the connection with certain diseases. All toxicants exert their initial influence at the cell membrane level whether the exposure is at the gut, skin or lung interface. Mickly et al (1997) determined that the common ion toxicity in membrane concentrate is not caused by the membrane process itself, but results from the nature of the groundwater. This statement could be applied to the facilities using RO membranes to treat the secondary wastewater for producing recycled water. The constituents in the secondary effluent (or in the mixture of primary and secondary effluent) could determine the constituents of the reject brine generated.

Several essential common ions play their physiological roles at elevated concentrations. Heavy metals can be quite toxic at very low concentrations, but can also contribute to physiological well-being at extremely low concentrations. It appears that heavy metals in low extracellular concentrations can exert very destructive influences on the integrity of the so-called tight junction between the cells. As heavy metal concentrations increase, osmo-regulation could be interfered with by impairing the salt accumulation, and by enlarging leak pathways through which solutes are lost to the environment (Mickly, 1997).

The RO membranes are very selective to inorganic constituents depending on their pore size. Nitrate is one of those inorganic contaminants. Nitrate contamination of water sources is a widespread problem in the United States and Europe. Although one might think that the problem arises from natural sources, the contribution to the problem by human activities can not be overlooked. Poor management of agricultural activities, improper discharge of human and animal wastes, and unregulated industrial processing operations are substantial contributors to increases in the nitrate concentration.

Waters and wastewaters containing nitrate cause eutrophication in receiving bodies as nitrate serves as one of the inorganic nutrients required along with phosphate. Eutrophication leads to severe water quality deterioration caused by increase in the algal growth and the concomitant oxygen depletion. In addition to eutrophication problems, nitrate also poses health hazards. Although the exact nature of nitrate toxicity to humans is not entirely understood, ingestion of water containing high nitrate and its consequent reduction to nitrite in the gastrointestinal tract produce methemoglobinemia or “blue baby syndrome” in infants (McLeaf and Schroeder, 1995). Furthermore, there are inherent fears that ingested nitrate and nitrite could be transformed internally into carcinogenic nitrosamines (Payne, 1981). Lastly, transformations

of nitrogen compounds by microorganisms lead to the production of gaseous intermediates such as nitric and nitrous oxides that are considered major contributors to ozone depletion in the stratosphere (Wang et al, 1995).

The conversion or discharge of nitrate is usually governed by environmental regulations pertaining to allowable concentration levels, and the economics of treatment technologies. The health problems associated with consumption of high-nitrate waters have forced regulatory agencies to establish maximum contaminant levels (MCLs). The U.S. Environmental Protection Agency has established MCL of 10 mg/l for nitrate in drinking water. Due to public health concern, waters contaminated with nitrate require adequate treatment prior to usage. The most common treatment technologies employed today are electrodialysis, distillation, ion exchange, reverse osmosis, and biological packed bed or fluidized bed processes.

1.2.2. Water Recycling in the Orange County Water District

Orange County Water District (OCWD) operates Water Factory 21, one of the most advanced water reclamation research facilities in the United States. The OCWD plans to utilize membrane technology for recycling water through the Groundwater Replenishment (GWR) System. Membrane processes have been considered because the plant is located in a settling area where there is little possibility of expansion. The OCWD initiated the GWR System with the objective of providing new local water supply to the community through groundwater recharge. In Orange County, a population of 2.2 million depends on groundwater resources towards meeting 65-75% of their water needs. About 40% of the total water demand is met by importing water. In order to meet the water demand for a growing population, it is imperative for the District to prevent the depletion of groundwater resources. It is for these reasons, the GWR System will provide sufficient recycled water to maintain the full groundwater resources of the region by groundwater recharge and injection. The first phase of the project planned to be completed by 2004 will produce 50,000 acre feet per year (afy) of recycled water, while the third phase planned for completion by 2020 will yield 110,000 afy.

The water recycling operations entail the application of advanced water treatment technologies at the Water Factory 21. These technologies include RO supported by microfiltration and ultrafiltration to demineralize the secondary effluent from the Orange County Sanitation District (OCSd). It is foreseen that when the membrane processes eventually replace

the conventional processes for water recycling, the brine concentrates originating from the RO units could cause significant environmental impact, as discussed earlier.

At the Water Factory 21 where this research is conducted, the main source of brine is the RO membrane process. The research RO plant produces about 6 mgd of recycled water. The process recovery of the RO membranes is approximately 85 percent, and 15 percent of the feed is discarded as brine, corresponding to an average brine flowrate of 0.9 mgd. The total dissolved solids (TDS) concentration in the brine is about 4000 mg/l, and the average ammonia concentration is 100 mg NH₃-N/l. Table 1.1 shows the characteristics of the OCWD RO membrane brine concentrate, with reference to various constituents and their concentrations. One problem with brines is that they contain high concentrations of ammonia, TDS and heavy metals that could have toxic effects on marine life upon disposal. Its concentrated constituents render it

Table 1.1. Reverse osmosis brine characteristics (obtained from Orange County Water District Laboratory; data collected from 7/31/1998 to 08/19/1999)

Constituent	Unit	Concentration	
		Min	Max
TOC	mg/l	31.4	44.9
Total Dissolved Solids	mg/l	3380	4430
Organic N.	mg/l	1.7	11.3
NH ₃ -N	mg/l	62.1	97.8
NO ₃ -N	mg/l	< 1	8.48
NO ₂ -N	mg/l	<4	9.3
SO ₄ ⁻²	mg/l	999	1450
PO ₄ ⁻³	mg/l	15	25
Cl ⁻	mg/l	800	1000
F ⁻	mg/l	0.5	1
CN ⁻	µg/l	-	40
Ca	mg/l	-	500
Mg	mg/l	-	50
Ag	µg/l	<1	5.2
As	µg/l	<2	19
Ba	µg/l	89	120
Cd	µg/l	<1	3.8
Co	µg/l	<1	3.6
Cu	µg/l	13	37
Fe	µg/l	260	710
Hg	µg/l	<0.5	1.4
Mn	µg/l	120	250
Pb	µg/l	<1	4.3
Se	µg/l	<5	7.3
Zn	µg/l	74	180

toxic to human, plant and animal life in spite of its small volumes. For instance, ammonia causes general deoxygenation, and is therefore poisonous for marine life. Furthermore, it increases the chlorine demand required for disinfection, as it forms chloramines with chlorine. Another adverse effect of ammonia is that it causes corrosion of industrial structures. Heavy metals tend to accumulate in the tissues of aquatic species and could be toxic even at very low concentrations. High total dissolved solids content could yield complexation reactions with metals, alter initial dilution or change the physiological reactions of marine organisms. High electrical conductivity of the brine concentrate is attributed to its high TDS level. Sulfate and chloride could be toxic to the environment into which it is discharged. In the OCWD, the brine is currently discharged into the ocean via an outfall.

1.2.3. Disposal Options, Environmental and Regulatory Issues in Handling RO Brines

As mentioned in the previous section, brine concentrate is considered non-recyclable due to its characteristics. Ocean dump, stream discharge, dilution, deep-well injection, evaporation ponds, and spreading on an arid land area are among the current trends for disposal. The disposal alternative chosen by the water authorities could be responsible for high concentrations of nitrogen compounds and heavy metal species in the surface waters, and could pose serious health risks and environmental problems.

The main concern associated with disposal of brine into surface waters is its impact on various beneficial uses. In assessing the impacts of brine disposal in marine waters, several issues have been identified. Among these issues are the toxicity concerns associated with concentrated TDS with elevated levels of heavy metals, and increasing toxic pollutants to levels which could result in violation of water quality standards, necessitating a need for source control. Brines usually contain high TDS that can complex with metals, and alter the initial dilution or change the physiological reactions of marine organisms. Three types of potentially toxic impacts to marine organisms are possible as a result of exposure to elevated contaminant levels in brine streams (OCWD Final Feasibility Study, 1995):

- Physiological impacts on the marine biota resulting from intermittent exposure to increased total dissolved solids and heavy metal content,
- Toxic effects resulting from brine discharge due to chemical additives or concentration effect,

- Stress effects leading to lower resistance of the endogenous organisms to other environmental factors that would otherwise not occur.

The best disposal alternative available today appears to be ocean discharge or discharge into a nearby water body. However, many recycling facilities that employ or plan to employ RO technology are often not situated near an ocean or available surface water for the ultimate disposal. Such facilities will need to find their own ways to handle or treat the brine prior to disposal.

The geographic location of the RO treatment plant dictates the type of disposal system that could be employed. For instance, Turner et al (1997) conducted a study for a two-stage low pressure RO pilot plant in a small, underdeveloped community in Texas. Prior to this project, the only potable resource providing potable water to this community was a groundwater that was highly saline due to salty water intrusion into the aquifer. The RO plant constructed upon the findings of this investigation provided exceptionally high quality water. However, the disposal of the brine concentrate became a major problem. After having considered many options such as self-sealing infiltration basins, salinity gradient solar ponds and saline vegetative wetlands, Turner and coworkers decided to construct enhanced evaporation ponds. Their decision favored by the availability of ample and inexpensive land area available. These researchers stated that disposing of the highly saline concentrate in semi-arid regions posed a considerable challenge in the sense that the selected disposal option should not be responsible for contaminating the surface water or groundwater resources. This was not only environmentally unacceptable but also economically and socially detrimental to communities that relied on those water resources. When membrane technology is chosen for treatment, methods to use the brine concentrate as a resource rather than a waste by-product should be sought.

The disposal of RO concentrates could be the deciding factor in site selection for the RO treatment facilities, as stated by Squire et al (1996). The brine concentrate they handled was high in alkalinity, sulfate, chloride, TDS, and trace and heavy metals. The contaminant species in the concentrate were approximately concentrated by five times during the RO process, and it constituted two percent of the overall RO feed volume corresponding to a process feed recovery of about 82 percent. After considering different disposal alternatives, they finally decided on surface water discharge due to proximity of the treatment facility to a near river, and contacted the local Environmental Agency to obtain an approval for river disposal. Since this disposal was

the first of its kind in the region, the agency showed great concern about the disposal due to the characteristics of the brine concentrate. Finally, it was concluded that the brine could only be discharged into the river after being diluted with the backwash water generated from the filtration unit. Since there were no established regulations pertaining to the brine concentrate, and no pre-established water quality data, the facility was required to monitor the river water quality for evaluating the long-term impacts of the disposal. Qudkirk and Carns (1997) supported the idea of diluting the RO concentrate brine with some kind of used water. Since dense brine discharge may impact the benthic environment co-discharges could be beneficial in diluting the brine.

Acquaviva et al (1997) concluded that concentrate disposal must be an integral part of RO treatment plant design, permitting, and operational considerations. Strict regulations pertaining to brine concentrate disposal can potentially present substantial economic burden for small and medium-sized systems. These burdens apply to both the planning of new systems and the continuing operation of existing systems. For example, the RO reject brine is regarded as an industrial waste by the U.S.EPA, and a discharge permit is required for its disposal in the state of Florida. Large municipal systems can handle their brines by constructing injection wells, whereas this option is not financially acceptable in the case of smaller treatment systems. Smaller systems could select other options such as surface water discharge and various types of land application systems.

Since membrane processes are fairly new in water recycling activities, there are no established regulations pertaining to the handling of RO brine concentrates. As membrane technology continues to evolve and become popular as an advanced water treatment and recycling technique, brine handling and disposal will become a substantial problem for most facilities. In the near future, new regulations may be enforced to preserve and protect marine environments from the adverse effects of improper disposal. The regulatory agencies may force the treatment plants to implement treatment techniques to treat their brine streams. Today, the research is intensified on finding new and cost-effective treatment alternatives to effectively handle brines at the source.

The research discussed in this report is mainly focused on brine handling via employing a biological treatment technique called Fluidized Bed Biofilm Reactors with Granular Activated Carbon (FBBR-GAC) to remove nitrogen compounds through denitrification.

1.3. Research Objectives

The main objective of this research is the removal of nitrogen compounds (nitrates and nitrites) from the RO membrane brine concentrate by using biological denitrification technique referred to as Fluidized Bed Biofilm Reactors with Granular Activated Carbon (FBBR-GAC) as the support medium for the denitrifying microorganisms.

The research focuses on assessing the feasibility and efficacy of the anaerobic FBBR-GACs technology for the denitrification of high nitrate and TDS brine streams generated from the RO membrane process in water recycling facilities. The contaminants to be removed are nitrogen species such as nitrates and nitrites. The research furthermore includes an evaluation of the effects of various environmental parameters such as temperature, pH, carbon to nitrogen ratio, and excessive salt concentration (total dissolved solids- TDS) on the process efficiency. This investigation is directed at optimizing the efficiency and economics of the FBBR-GAC treatment system.

The research also includes the application of mathematical model to predict the performance of anaerobic FBBR-GAC process. The development of a modeling and design protocol provides the basic design tools for process up-scaling. Bench-scale experiments determine several model input parameters. These include adsorption parameters, biokinetic parameters, and axial dispersion coefficient. Other necessary parameters such as column film transfer coefficient, biofilm thickness, etc. are estimated by correlation techniques or direct measurements. The predictive capability of the model is verified by comparing the model outputs with the results from bench-scale FBBR-GAC studies. The model will then be up-scaled to predict the performance of pilot and full-scale versions of the process.

The final objective of this research is to investigate the efficiency of the FBBR-GAC process in removing sulfate along with nitrate removal from the nitrified RO brine concentrate. The discharge of rich sulfate content of RO brines also renders them hazardous to the environment. In order to achieve simultaneous reduction of nitrate and sulfate, it is necessary to find the optimal conditions such as the retention time, the amount of GAC used, carbon source utilization, etc.

1.3.1. Scope

1. Conduct bench-scale biokinetic studies to determine the effects of temperature, pH, carbon to nitrogen ratio, and high TDS concentration on the biological denitrification process,
2. Choose the optimum parameters from (1) to conduct the biokinetic experiments to obtain the Monod biokinetic parameters,
3. Conduct equilibrium adsorption studies for nitrate to estimate the carbon adsorption capacity and intensity parameters,
4. Conduct adsorption rate studies by using specially designed reactors in order to determine the mass transfer parameter, i.e., surface diffusion coefficient,
5. Conduct anaerobic FBBR-GAC studies to determine the process performance in removing nitrate,
6. Apply a mathematical model for the design and up-scaling of the denitrification FBBR-GAC process for the removal of nitrogen compounds from the RO concentrate brines,
7. Conduct further FBBR-GAC studies to verify the predictive capability and applicability of the mathematical model,
8. Conduct FBBR-GAC studies to investigate the process efficiency for simultaneous removal of nitrate and sulfate.

2. PROJECT APPROACH

2.1. Theory and Rationale

Fluidized bed biofilm reactors (FBBR) are upflow reactors designed on the principle that the support medium in the reactor provides a means of attachment for microorganisms. The attached microorganisms grow and form biofilms that are effective in the degradation of substrate in the feed water or wastewater. The feed is passed upward through the bed at a flow velocity sufficiently high to cause bed expansion or fluidization beyond the point at which the frictional drag force is balanced by the net downward gravitational force. The bed is kept in fluidized condition by either high influent flowrates or high recycle ratios to approach completely mixed flow regime.

Anaerobic FBBR-GAC process offers many advantages over the other conventional treatment processes. Among these advantages are (Mulcahy and Shieh, 1987; Sutton and Mishra, 1991; Delanghe et al, 1994):

- The main advantage of the FBBR-GAC process with recycle is a reduced reactor size made possible by the efficiency associated with the development of a high biomass concentration. Site availability in densely populated areas presents a serious obstacle to the treatment plants that are trying to meet the current or predicted effluent nitrogen requirements with conventional fixed-film or suspended growth technologies. The FBBR-GAC process holds promise for meeting space requirements and the low-level nitrogen removal objective.
- The FBBR-GAC process with recycle can provide approximately five to ten times the microorganism concentrations as compared to suspended processes. Beyond the point of minimum fluidization, the media particles provide a vast surface area for the biological growth, in part, leading to the development of a biomass concentration five to ten times greater than that normally achieved in many conventional bioreactors such as activated sludge reactors. The superficial upflow velocity of the reactor, media size and density, biofilm thickness, and biofilm moisture content are among the most important factors that affect the biomass concentration.
- The microorganisms in the FBBR-GAC process appear to be relatively resilient. For example, denitrification resumes immediately when the unit is placed back on-line following a period of plant shut-down for maintenance.

- The FBBR-GAC process is relatively simple to operate and maintain. Once initial start-up problems are resolved and the reactor bed is established, the system requires minimal operator attention. Process control techniques (principally ethanol feed and bed control) are simple and routine once the system reaches equilibrium and the staff gains familiarity and confidence with the system.
- The process affords low capital cost and operational problem.

This research employs the FBBR-GAC process with recycle for the treatment of nitrate in pre-nitrified reverse osmosis brine. The process offers three distinct advantages: (i) the polluting nitrate is actually removed, not concentrated, (ii) the process does not produce large amounts of troublesome waste by-products such as regeneration brines, and (iii) nitrate concentration of brine is suitable to be removed by biological denitrification process. Figure 2.1 shows the schematic of the FBBR-GAC technology for the nitrification and denitrification of RO brine.

Although the FBBR concept and its advantages over the other conventional technologies had been realized for a long time, there were no known full-scale plants in operation until 1980s. The technology had been studied extensively only on the laboratory and pilot scale until 1983 (Heijnen et al, 1989). After overcoming the operational constraints such as unstable process, low reactor capacity, and small substrate spectra, FBBRs have become more widespread, and constructed and operated successfully in full-scale systems since 1984. The result of these studies and operations has been that anaerobic FBBR technology has proven to be as a suitable process for wastewater treatment (Godia and Sola, 1995).

After the development of the FBBR process, there has been considerable amount of research on denitrification to investigate different aspects of the process, and to develop models that would greatly aid process design. Yoder et al (1995) summarized the most important parameters in the modeling and design of FBBRs as: (i) superficial velocity, (ii) the quantity of biomass and biofilm thickness, (iii) expansion in bed height due to hydraulic flow and biofilm growth, (iv) expansion index and expanded bed height, (v) type, size and density of the support media used, and (vi) cross sectional area of the reactor.

The type, size and density of the support media and the cross sectional area of the reactor is usually chosen during the design step. However, the biofilm thickness and expanded bed height

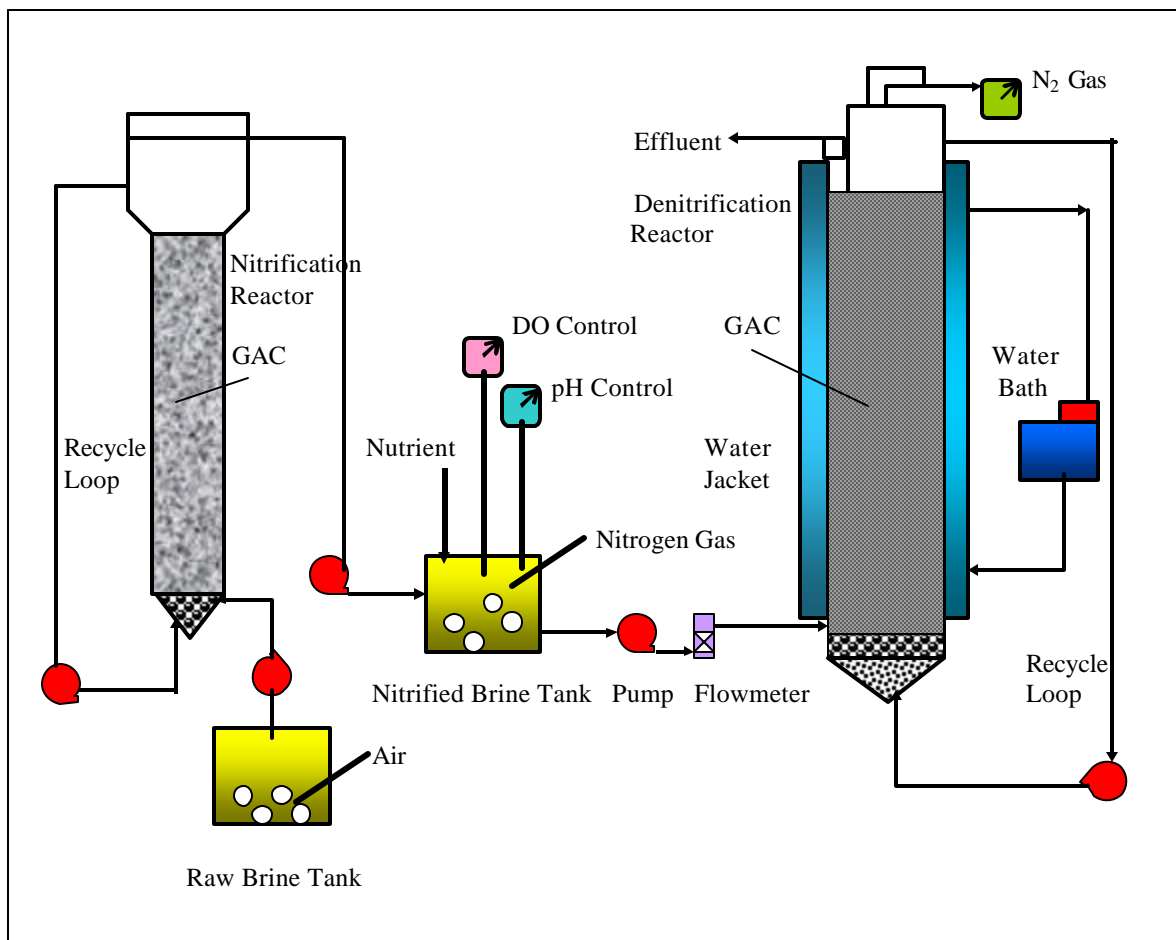


Figure 2.1. Schematic of the FBBR-GAC nitrification and denitrification process

which affect the fluidization biomass concentration during the operation are calculated by using correlation equations or by laboratory or pilot scale experiments. Research has been focused on finding correlations among these parameters that serve as a basis for system optimization. The general operating rationale is to introduce the feed to the FBBR without any pre-treatment, and have a near-zero nitrate discharge in a bioreactor of reasonable length.

A simplified mathematical model developed by Mulcahy et al (1980) for a FBBR denitrification process using glass beads assumed three important steps: (i) transport of substrate from bulk-liquid to liquid-biofilm interface (external mass transfer) (ii) transport of substrate within the biofilm (internal mass transport), and (iii) substrate conversion reaction within the biofilm. These researchers developed the model by using both zero order and first-order kinetics. They concluded that external mass transfer and axial dispersion were not highly significant in the FBBR operation. According to these investigators, the biomass concentration could be predicted from superficial velocity, expanded bed height and support media type and volume.

Shieh (1980) investigated various parameters affecting the denitrification performance of FBBRs, and used some data gathered from several different treatment facilities to verify the mathematical FBBR model that he proposed. He assumed that the substrate conversion reactions followed intrinsic zero-order kinetics, and were limited by the diffusion of the substrate within the biofilm. He also assumed that the internal mass transfer resistances were such that the substrate penetrated only partially into the biofilm. After conducting several FBBR experiments, he concluded that biofilm thickness and media size were the two most important parameters affecting the process performance. An optimal value existed for each of these parameters under a given set of operating conditions that maximized the substrate conversion rate. Similar conclusions were drawn by the same author at a later date as a result of similar experimental work (Shieh et al, 1981).

Another study conducted by Narjari et al (1984) investigated the effect of superficial velocity on the removal of nitrates as well as on the growth of biomass in a FBBR that utilized sand particles. Initially, there was a steep decline in the effluent nitrate concentration with time, but eventually the concentration approached a steady state value. The nitrate removal reached a maximum at a specific superficial velocity, and at this velocity the stable biofilm thickness also reached a maximum. When the superficial velocity was increased, the biofilm thickness

decreased due to increased drag, and more importantly due to the shear on the bioparticles as well as sloughing between them.

Similar models have been proposed by many other researchers (Hancher and Perona, 1982; Boaventura and Rodrigues, 1988; Lin, 1991; Kim, 1992). In all these models, the biofilm kinetics were assumed to be either zero or first order, or based on Monod equation. Boaventura and Rodrigues (1988) developed their models based on the reaction scheme of two consecutive zero-order reactions ($\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{Products}$). These investigators distinguished three regimes arising from the competition between the reaction and transport of nitrate and nitrite species inside the biofilm. Their model also incorporated mass transport of nitrates and nitrites by diffusion into the biofilm. In another study, Kim (1992) assumed that Monod kinetics would apply to his FBBR system, and provided solution to his proposed model by using the one-point orthogonal collocation method. His model could be used for the FBBR systems in which the biofilms were "shallow" or thin. LaMotta and Cascante (1996) showed that zero order approximation provided adequate description of anaerobic substrate consumption in an experimental FBBR denitrification operating under a wide range of effluent concentrations. They proposed a simple correlation between influent and effluent substrate concentrations, stating that the complete penetration model for nitrate proved better than the partial penetration model. In addition to these researchers, Williamson and McCarty (1976) also concluded that the substrate utilization involved simultaneous molecular diffusion and biochemical reaction governed by Monod kinetics.

There is a strict correlation between FBBR biofilm density and biofilm thickness in an FBBR-GAC process. As indicated by Ro and Neethling (1991), the biofilm density in a FBBR is not constant, but decreases as the biofilm thickness increases. Therefore, a thicker biofilm will form a larger but less dense particle. This finding is important in order to understand the interactions between the particle characteristics and particle settling velocity, a critical parameter in design and operation. The less dense bioparticles will cause excessive bed expansion and move to the upper part of the reactor. With a high superficial velocity, these low-density bioparticles may leave the reactor with the effluent or recycle flow. This could cause operational problems such as clogging in the pipes and pumps as well as poor treatment efficiency and unstable effluent concentrations. In order to prevent this, most FBBRs are designed with the necessary mechanical equipment such as growth control pumps, air scouring and/or mixing device that automatically

starts functioning when the expanded bed height reaches a pre-marked level. Thus, the excessive biomass is slaughtered off from the support media and wasted.

2.2. Activated Carbon as Support Medium in the FBBR-GAC Process

The selection of support media type is an important means by which biofilm thickness and biomass concentration in a FBBR could be controlled. Use of larger and denser support media while maintaining the superficial velocity, expanded bed height and support media volume constant throughout the operation results in increased equilibrium biofilm thickness. Increasing the biofilm thickness or the support media volume gives rise to increased biomass concentration in the reactor (Mulcahy and Shieh, 1987).

Several researchers have used different types of support media in their reactors, and compared the system performances. Among these media, activated carbon is an excellent adsorbent with its large surface area, high degree of surface reactivity, universal adsorption affinity, and favorable pore size and structure, which makes the internal surfaces accessible. Adsorption takes place in the micropores contained in the specific surface area of the order of 800-1500 m²/gr (Bansal et al, 1988). In another study, Pirbazari et al (1990) compared the ability of various natural and synthetic media such as ion-exchange and carbonaceous resins, sand and GAC in supporting biomass growth. The comparison revealed that GAC supported a much richer biological growth than the other media. Treatment systems with activated carbon also appeared to be more resistant to shock loadings and toxic contaminants (Pirbazari et al, 1989; Kim and Pirbazari, 1989).

Coelhoso et al (1992) compared the denitrification results in FBBR process employing activated carbon and sand. It was observed that the average cell residence time for activated carbon particles was much lower than that for sand particles. Furthermore, the quantity of nitrate consumed per quantity of biomass in the activated carbon FBBR was substantially larger than in the FBBR with sand particles. Also, the biomass yield was three times greater in FBBR with activated carbon than the FBBR with sand. They concluded that FBBRs utilizing activated carbon as the support medium for the biomass growth had much more homogeneous biomass spatial distribution than those using sand as the support medium.

FBBRs could use a variety of support media such as sand, coal, synthetic media, and activated carbon. This research employs granular activated carbon as the support media as it has several distinct advantages over the other media (Ying, 1978; Weber et al, 1979; Rice and

Robson, 1982; Pirbazari et al, 1990; Nakhls and Suidan, 1995; Sison et.al, 1996), as described below:

- Good adsorbitive characteristics and relatively rough surface topography of carbon particle act as a shelter for the bacteria from high fluid shear forces while providing a favorable microenvironment for microorganisms in terms of substrate and nutrient concentrations. Consequently, the biofilms appear to be thicker and denser than those maintained on other inert support media.
- Carbon can effectively remove toxic metals from the solution and therefore minimize the inhibition effect on biofilm.
- Bioregeneration in GAC, a process where previously adsorbed organic material is removed through biological activity leading to the re-opening of the adsorption sites, is also a significant property of carbon. In actual conditions, nitrate concentration in the wastewater to be treated may vary with time. In such cases, denitrification systems with external carbon supply may become costly because excess organic carbon should be added all the time, or precise control of addition of organic carbon should be implemented to ensure stable nitrate levels in the effluent. Aside from high operating costs, the high residual carbon concentration in the effluent during periods at low influent nitrate concentrations poses another major problem. The adsorption and desorption capability of carbon can provide advantages under such circumstances because GAC can be used as storage medium for the excess organic carbon when the influent nitrate concentration is low.
- Start-up of the process becomes relatively easy. It can be operated in batch mode initially. Furthermore, it can withstand shock loads with respect to toxic components and flow rates. Lastly, it can reach steady state quickly as a result of rapid microbial acclimation.

2.3. Modeling the FBBR-GAC Process

2.3.1. Process Bioadsorber Models

Mathematical models have been developed for processes employing GAC after extensive studies and experimentation. Ying and Weber (1979) developed a model that included liquid film transfer, intraparticle diffusion, Monod kinetics for substrate utilization and biomass buildup. The biofilm thickness was considered to be a function of both time and distance into the bed, and it kept growing until it reached a certain thickness that was maintained the same by washing the

media and air scouring. Their model was applicable to both completely mixed and plug flow fluidized beds, and had good predictive capability for glucose and sucrose as the substrate.

Andrews and Tien (1981) presented a model for the biological activity in fluidized beds based on completely mixed tank assumption. The model included the following phenomenological assumptions (i) mass transfer resistance of the liquid film and diffusion resistance of the solid phase were negligible (ii) organic material was assumed to be present in low concentrations to limit the biomass growth, and (iii) organic material consumption by biofilm was assumed to follow first-order kinetics. Their model exhibited satisfactory predictive capability with respect to the organic material they used at dilute concentrations. Nonetheless, due to the restrictive nature of the assumptions the applicability of the developed model to denitrification process is limited. Subsequently, Speitel et al (1987) and Chang and Rittmann (1987) proposed similar models as Andrews and Tien (1981). The Chang and Rittmann (1987) model was for a completely mixed FBBR while Speitel et al's (1987) model was for plug-flow fixed bed configurations. In essence, both models were efficient in predicting the effluent concentration of a single substrate (phenol) in low concentrations.

However, it is necessary to introduce a better model that would assume that contaminants could be present in high concentrations. Furthermore, the mass transfer resistance can not always be negligible when the substrate concentration is high. Recycling should also be taken into account since, in some operations, in order to alleviate the bed clogging and pressure drop problems, to increase the extent of mixing, to prevent the bioparticle agglomeration and to increase the shear inbetween the particles high recycle ratios could be employed. Pirbazari and coworkers (Kim and Pirbazari, 1989; Ravindran et al, 1997) developed a model for the recycle fluidized bed (RFB) adsorber configuration. This model, which incorporated additional features such as maximum biofilm thickness, will constitute the framework for the proposed model.

2.3.2. Proposed Model Milieu and Assumptions

The design of FBBR-GAC process necessitates prior modeling efforts in order to estimate the performance, feasibility and cost of the process. In other words, the cost-effective design and economic performance evaluation of FBBR-GACs are essentially predicated upon the application of phenomenological models. A mathematical model that combines the estimation of overall removal of nitrate and biodegradation as well as adsorption would be a useful tool for the design engineers in up-scaling the process from bench scale to pilot scale and eventually full

scale. A good model makes it possible to determine the size of the reactor of interest, and to predict the influence of changing the operating conditions on the reactor performance. The input parameters required by these predictive models are obtained from well-designed bench scale experiments, a technique that reduces the need for expensive and time-consuming pilot scale investigations. A mathematical model that has been proven to be successful facilitates pilot scale investigations and a better understanding of various phenomena and associated interaction mechanisms among microorganisms, substrate and support particles.

The first step in developing a conceptual model involves understanding its essential components. Figure 2.2 shows a segment of a fluidized bed biofilm column formulation for the model. As demonstrated, microorganisms attach themselves onto the activated carbon surface and begin to grow. Initially, the biofilm is very thin, and if the substrate is adsorbable, much of it is transported and becomes adsorbed on to the particle surface. The model described herein considers adsorption as well as biofilm degradation phenomena (Kim, 1987; Kim and Pirbazari, 1989; Ravindran et al, 1997). However, the preliminary bench-scale adsorption studies showed that nitrate is very weakly adsorbed onto the GAC. This necessitates a modification of the current model by excluding the adsorption phenomenon.

The model incorporates the following fundamental mechanisms: (i) substrate transport from bulk liquid to biofilm through an external liquid film, (ii) mass transfer and degradation within the biofilm, (iii) adsorption (if any) within the activated carbon particle, and (iv) growth of biofilm.

The important assumptions made for the development of the model are as follows:

1. The activated carbon particles are spherical and uniformly distributed,
2. The FBBR has uniform cross sectional area,
3. The biofilm is homogeneous (its composition, density, porosity, and thickness, do not vary as the biofilm gets thicker), and it grows with time,
4. Adsorption of substrate (if any) onto the activated carbon particles is a reversible process (desorption),
5. The biodegradation kinetics and substrate utilization can be represented by Monod equation,

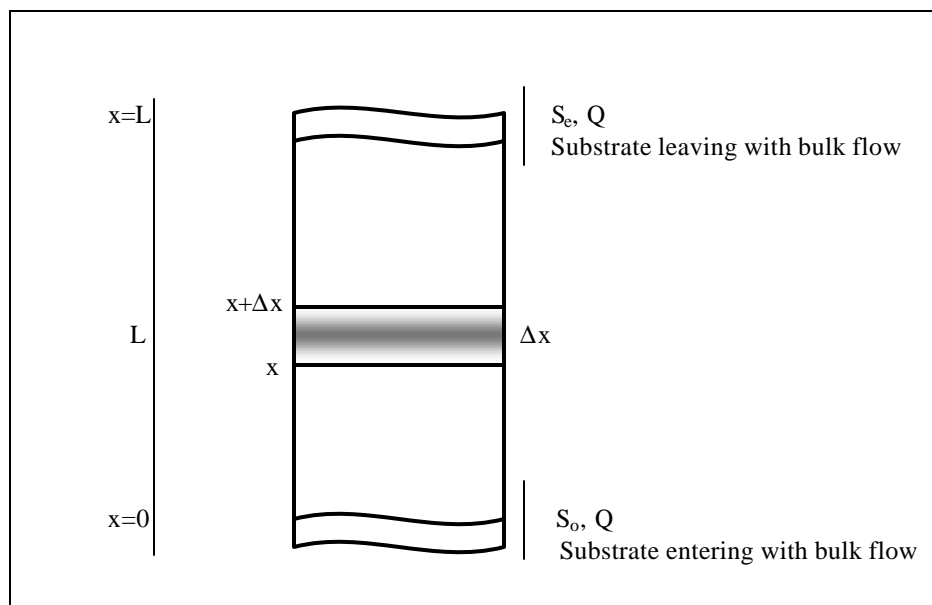


Figure 2.2. Schematic of a segment of FBBR-GAC column used in the formulation of the model

6. Biodegradation occurs only in the biofilm layer, and is negligible in the liquid phase; no biodegradation occurs in the activated carbon particle,

7. The substrate concentration profile across the biofilm can be considered to be in pseudo-state even though the biofilm thickness varies as a function of time,

8. The biofilm growth does not substantially affect the porosity of the fluidized bed, nor does it affect the flow pattern of the liquid. Especially during early stages of FBBR run, change in bed porosity due to bacterial growth is negligible (this assumption is essential for model development),

9. The biomass loss due to fluid shear from high superficial velocities in the bed is negligible during the initial stages when the biofilm is still thinner. However, the loss of biomass due to shear and decay balances the new biomass so that a steady-state maximum biomass concentration is reached within the bed,

10. The contribution of surface diffusion is more important than pore diffusion, and so pore diffusion is neglected,

11. The axial dispersion of substrate in liquid phase is negligible due to the higher degree of mixing,

12. The mixing and fluidization in the FBBR is achieved by high recycle ratios and upflow velocities,

13. The uptake of substrate by the activated carbon particle involves a two-step mass transport mechanism, namely the liquid film mass transfer followed by biofilm diffusion, and intraparticle solid phase diffusion (surface diffusion),

14. The model accounts for the effect of substrate diffusion through the biofilm and the associated mass-transfer resistance, an important aspect.

2.3.3. Formulation of FBBR-GAC with Recycle

For the substrate uptake by a biofilm in media-supported reactors, substrate must first be transported from the bulk fluid into the biofilm. This process may occur in three steps: (i) transport of substrate from the bulk fluid to the fluid-biofilm interface (external mass transfer), (ii) transport of substrate within the biofilm (internal mass transfer), and (iii) substrate

consumption reaction (biodegradation) within the biofilm. Figure 2.3 depicts the schematic of the components that will be used by the model.

a. Liquid Phase Material Balance

The material balance of the substrate (nitrate) for any differential segment of the bed is represented by the following equation:

$$\frac{\partial S}{\partial t} = D_x \frac{\partial^2 S}{\partial x^2} - v_x \frac{\partial S}{\partial x} - \frac{3k_{fc}(R+L_f)^2}{R^3} \frac{1-e}{e} (S-S_{fs}) \quad (2.1)$$

The boundary conditions for this equation are as follows:

$$S(x, t=0) = 0 \quad (2.2)$$

which assumes that there is no substrate in the liquid phase within the fluidized bed reactor at the time zero.

$$S(x=0, t) = \frac{QS_o + Q_r S(x=L, t)}{Q + Q_r} \quad (2.3)$$

The above equation assumes that the substrate concentration at the reactor entrance is non-zero due to the recycled flow.

b. Solid Phase Material Balance in Carbon Particle

The intraparticle substrate transport from the liquid phase into the activated carbon particle (adsorbent) is governed by the Fick's Law. The following equation assumes spherical symmetry of the adsorbent and diffusion in the radial direction:

$$\frac{\partial q(r, t)}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left(r \frac{\partial q(r, t)}{\partial r} \right) \quad (2.4)$$

whose initial and boundary conditions are as follows:

$$q(0 \leq r \leq R, t=0) = 0 \quad (2.5)$$

$$q(r=R, t) = q_s \quad (2.6)$$

$$\frac{\partial q(r=0, t \geq 0)}{\partial r} = 0 \quad (2.7)$$

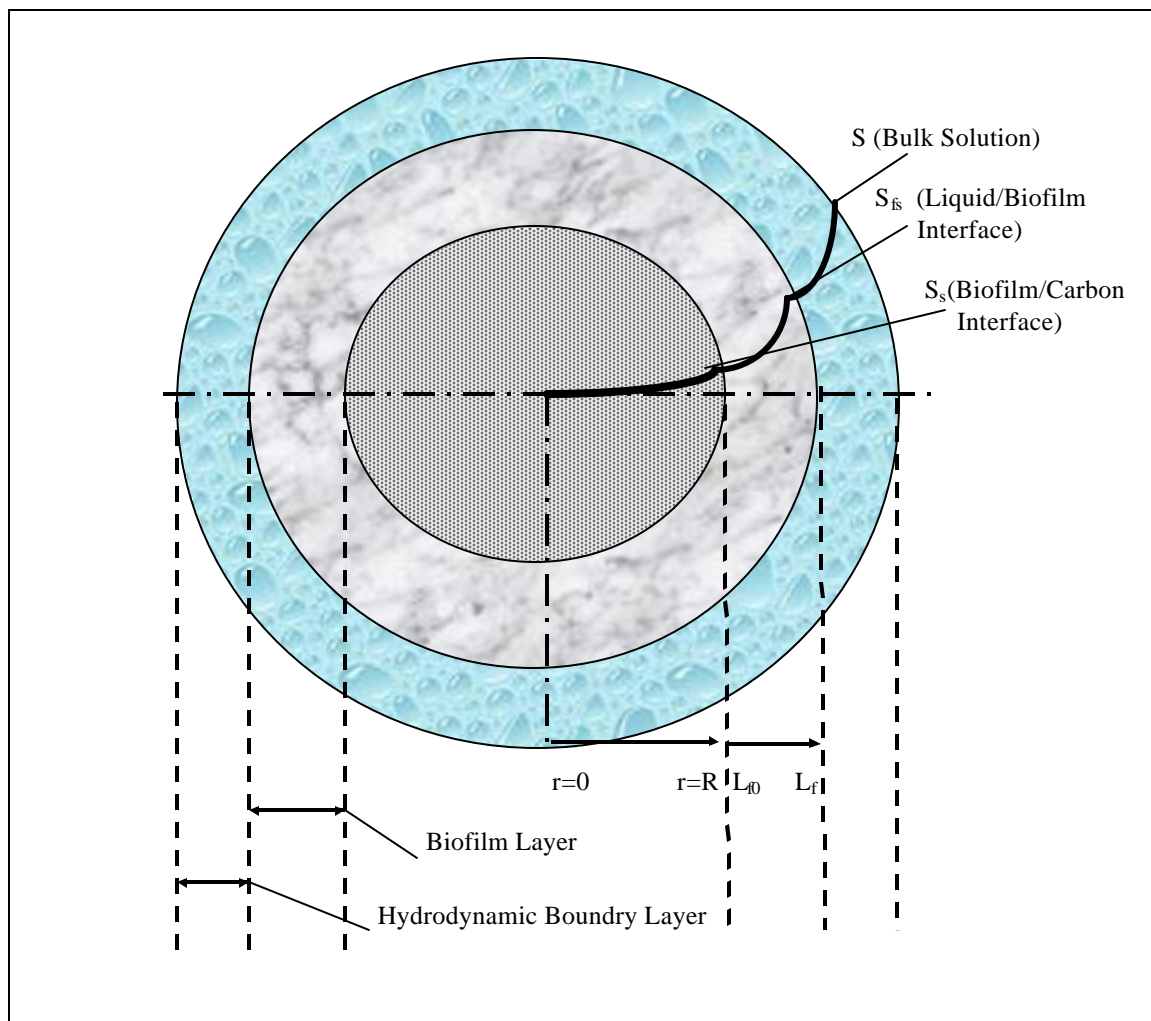


Figure 2.3. Substrate transport into the activated carbon bioparticle

Another mass balance equation is represented in the partial integro-differential form for the volumetric accumulation of the substrate within the carbon particle. This could be found by subtracting the rate of substrate degradation within the biofilm from the rate of transport from the bulk liquid phase:

$$\frac{\partial}{\partial t} \int_0^R q(r,t) r^2 dr = \frac{QR^3 k_f}{3V_a r_a} \{ (S - S(x=L,t)) \} - \frac{R^2 m_m X_f L_f}{r_a Y} \frac{S_{f,avg}(x,t)}{K_s + S_{f,avg}(x,t)} \quad (2.8)$$

c. Diffusion and Reaction in Biofilm

The following equation assumes that the substrate concentration within the biofilm layer changes only in the direction normal to the surface of the biofilm (z-direction). Also, the substrate concentration gradient across the biofilm is assumed to have reached pseudo steady state.

$$\frac{\partial S_f(x,r,t)}{\partial t} = D_f \frac{\partial^2 S_f(x,r,t)}{\partial r^2} - \frac{m_m X_f}{Y} \frac{S_f(x,r,t)}{K_s + S_f(x,r,t)} \quad (2.9)$$

for

$$r = R + L_f \quad (2.10)$$

The boundary conditions are:

$$S_f(x, r = R, t) = S_s(x, t) \quad (2.11)$$

and

$$S(x, r = R + L_f, t) = S_{fs}(x, t) \quad (2.12)$$

d. Growth of Biofilm

The variation of the biofilm thickness with time and position could be represented by the following equation, wherein Monod kinetics describe the biofilm growth and decay.

$$\frac{\partial L_f(x,t)}{\partial t} = \frac{m_m S_{f,avg}(x,t)}{K_s + S_{f,avg}(x,t)} L_f(x,t) - k_d L_f(x,t) \quad (2.13)$$

The initial and boundary conditions are as follows:

$$L_f(x, t = 0) = L_{f0} \quad (2.14)$$

and

$$L(x, t = t_{\max}) = L_{f, \max} \quad (2.15)$$

e. Adsorption Equilibrium Relationship

The Freundlich isotherm model relates the equilibrium solid phase substrate concentration to the liquid phase substrate concentration near the carbon particle surface.

$$q_s(r = R, x, t) = K_F S_s^n(x, t) \quad (2.16)$$

where K_F and n are constants to be found via experimental studies.

2.3.4. Non-Dimensionalization and Numerical Solution to the Model

In order to be able to solve the above equations by using some numerical techniques, non-dimensionalization is essential. It is convenient to normalize the domains of variables between zero and unity, and express all the differential equations as well as their initial and boundary conditions in a systematized and compact form. Moreover, by non-dimensionalization, the equations can be handled more easily, and numerical techniques could easily be applied. The transformation also provides more information on the convergence, consistency and stability of the numerical methods used.

The non-dimensionalized equations describing the overall phenomena that take place in the FBBR-GAC are too complicated to be solved analytically. Therefore, it is necessary to use appropriate numerical methods to solve them. This model could be solved by employing a hybrid technique that combines orthogonal collocation and Crank-Nicholson finite differences method. This combination has been proven very efficient as observed by Pirbazari and coworkers (Kim and Pirbazari, 1989; Ravindran et al, 1997). In this technique, the fluidized bed equations and the adsorption equations are approximated by the orthogonal collocation grids. The biofilm degradation and diffusion phenomena are computed by the Crank-Nicholson finite differences scheme. Two different numerical techniques are combined because orthogonal collocation method works best for spatial approximations when the solution to the problem does not have steep gradients, while finite differences method is more appropriate for the functions with steep gradients. The theory of orthogonal collocation method and its applications to solving the diffusion and reaction equations could be found elsewhere (Villadsen and Stewart, 1967; Finlayson, 1972; Jain, 1985). The partial differential equations in the model are first transformed

into ordinary differential equations, and then solved by using the GEAR software (Gear, 1971; Gear, 1976).

2.4. Nitrification Columns

In order to provide sufficient nitrified brine for the FBBR-GAC feasibility studies, two nitrification reactors of 2.4-L capacity each were employed as shown in Figure 2.4. The reactors consisted of two sections of different dimensions. The top section was 16 in diameter x 6 in length while the bottom section was 2 in diameter x 20 in length. The upper wide portion served as a reactor, and housed the recycle line and effluent port. The GAC was charged into the reactor in the bottom portion of the reactor. The top of the reactors was covered with plastic caps, which made it easy to collect samples. These reactors were able to provide a nitrified effluent flow of 16 to 20 ml/min. The corresponding hydraulic retention times (HRTs) were 4 hrs and 5 hrs, respectively.

Before charging the reactors, the GAC was washed several times with distilled water in order to wash out its powder content, and then dried at 105°C overnight. A 2 in layer of glass beads was placed in the bottom of the reactors to ensure uniform flow distribution. The reactors were subsequently charged with 250 g of GAC initially corresponding to a height of 7 in. After final fluidization, the GAC bed reached to a height of 12 in. The raw brine was collected in a 2-L flask. Sodium thiosulfate and phosphate were added as de-chlorinating agent and supplemental nutrient, respectively. The thiosulfate solution was prepared according to Standard Methods (1995). The phosphate solution was prepared by using a mixture of sodium phosphate and potassium mono phosphate, and fed into the reactor at a rate such that it did not constitute a limiting factor. The contents of the flask were aerated through air diffusers at all times to provide enough oxygen for biological activity. Both reactors were aerated with diffusers in the top portion where the recirculation line was connected to enhance the fluidization, and to maintain the dissolved oxygen levels above 5 mg/l.

The reactors were initially run for a few hours with brine to wash out the powder portion of the GAC, and to equalize the pH of the system. Then, both reactors were inoculated with a mixed bacterial culture obtained from a municipal wastewater treatment plant's aeration tank. The reactors were run in recycle mode for about three weeks to get the bacteria acclimated and attached onto the GAC particles. The bacterial growth was kept under control by regularly cleaning the walls of the reactors. The stability of the system was checked regularly by measuring

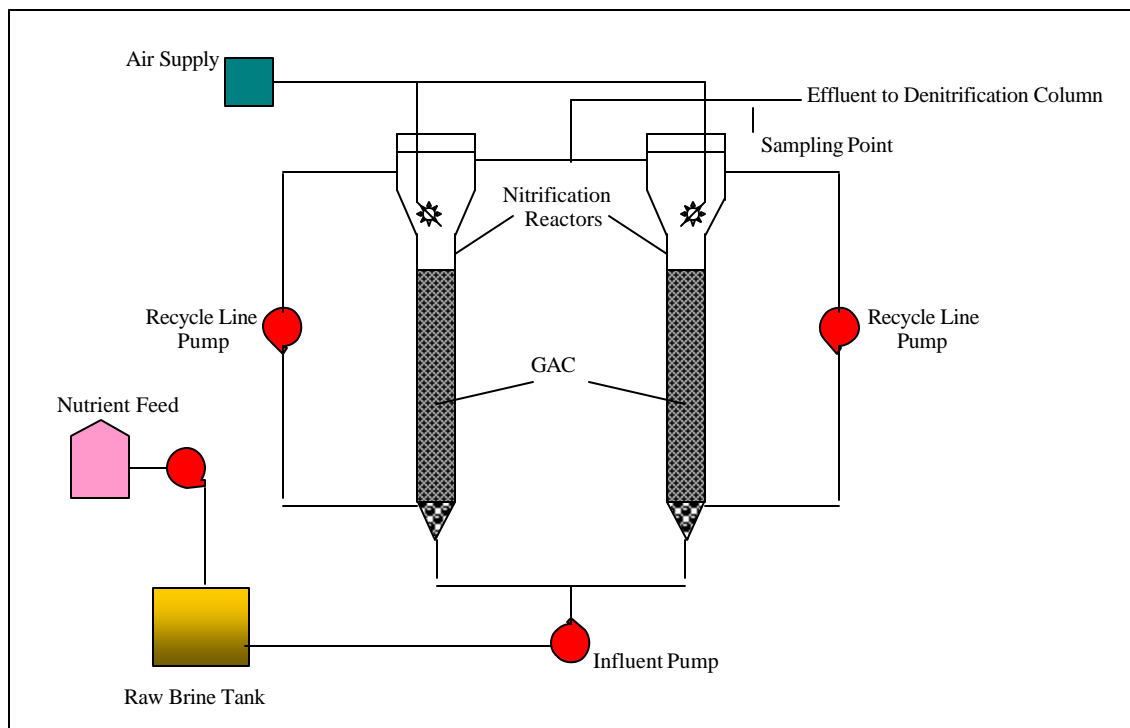


Figure 2.4. Schematic of the laboratory scale nitrification columns

the influent and effluent ammonia concentrations. The nitrification efficiencies achieved exceeded 95 percent during the course of this study. There was no nitrite accumulation throughout the experimental run. As soon as the steady-state ammonia removal was reached, the denitrification system was placed online.

2.5. Preliminary Denitrification FBBR-GAC Feasibility Studies

The 2-L denitrification reactor was constructed from plexiglass, and was of 2 in diameter x 3.3 ft in length as shown in Figure 2.5. In order to maintain constant temperature, the reactor was coated with a water jacket filled with 30°C water supplied by a water bath. Glass beads were placed on a perforated tray placed at the entrance port to provide a uniform flow distribution. The recirculation line and the feed line were provided with Masterflex pumps (Cole Parmer Instrument Co., Illinois). The reactor was designed in such a way to allow the nitrogen gas generated to exit the reactor through a gas flowmeter. The fluid flows were all controlled through flowmeters. Backflows were prevented by means of check valves. The reactor was charged with 320 g of GAC initially corresponding to a height of 11 in. After final fluidization, the GAC height reached 20 in (fluidization was achieved step by step not to wash out the attached biomass).

A 3-L capacity glass bottle was used to feed the nitrified solution to the denitrification reactor. The bottle was tightly capped, and its contents continuously purged with nitrogen gas in order to keep the dissolved oxygen concentration below the 0.2 mg/l level as specified in the literature. The cover of the feed reservoir was provided with ports that allowed the addition of nutrients (mainly phosphate), carbon source (mainly ethanol), and acid/base ($\text{H}_2\text{SO}_4/\text{NaOH}$) depending on the pH. The pH of the solution was automatically monitored, and supplemental phosphate was continuously replenished. High purity ethanol was fed into the feed reservoir at a rate of 2 ml/min to maintain a C:N ratio of 2:1 (mol/mol).

The reactor was operated with the nitrified influent for a few hours to clean the GAC of its powder content generated by attrition. It was subsequently inoculated with the anaerobic bacterial culture obtained from a wastewater treatment plant's batch tank when it was in its anaerobic cycle. Addition of brine was accompanied with the addition of excess amount of ethanol to enhance the growth of the biomass. After a short acclimatization period, the GAC particles were covered with a visible biomass layer. Subsequently, feeding with the nitrified brine

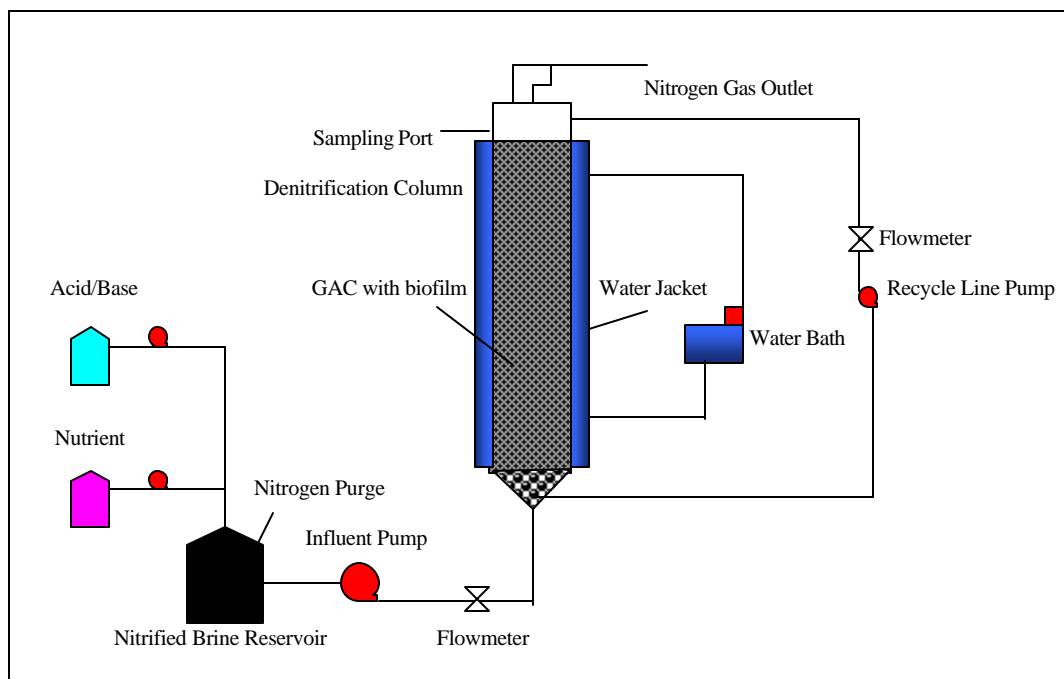


Figure 2.5. Schematic of the laboratory scale denitrification column

was initiated at 16 ml/min, which corresponded to a hydraulic retention time of 125 minutes. The reactor was able to provide full denitrification at all times for a period of 5 months.

After a few weeks of operation, the presence of hydrogen sulfide (H_2S) was detected in the reactor off-gas. It appeared that sulfate-reducing bacteria grew on the top few inches of the GAC bed, converting the sulfate content of brine to H_2S .

2.6. Batch and Chemostat Studies

All batch and continuous flow chemostat experiments were conducted in a BioFlu IIc Batch/Continuous Fermentor (Boston, MD). The chemostat of the fermentor was constructed of glass with a capacity of 1.5-L (1.3-L working volume), a built-in pH control electrode, a dissolved oxygen electrode, and an agitator with D.O. control. The apparatus was also equipped with a delivery system for acid, base, nutrients and feed water. The temperature was maintained at a pre-set level through a built-in circulating water bath.

The optimal temperature, pH and C:N ratio for the denitrification process was obtained from batch chemostat tests. For this purpose, a series of batch experiments were conducted using varying temperatures of 10, 15, 20, 25, 30, 35, 40 and 45°C and pH values of 6, 6.5, 7, 7.5, 8, 8.5 and 9. Similarly, different C:N ratios of 1.20:1, 1.52:1, 1.85:1 2.20:1 were employed to identify the optimal ratio, and the effect of TDS was evaluated with different levels corresponding to 4000, 8000, 15000 and 25000 mg/l. For each set of experiments, only one parameter was varied, and the other environmental conditions were maintained constant. For example, solution in the fermentor vessel was deoxygenated with nitrogen gas and agitated at 400 rpm at all times. An acclimatized denitrifying bacterial culture was used in all these experiments.

The biokinetic parameters, μ_m (maximum specific growth rate), K_s (half saturation constant), Y (yield coefficient), and k_d (decay constant) were determined by employing a series of continuous flow chemostat experiments. The brine feed was initially deoxygenated with nitrogen gas so that the dissolved oxygen level was maintained at less than 0.5 percent saturation at all times to promote anaerobic conditions. The agitation in the chemostat using a mixing fan operated at 400 rpm. At the start of each experimental cycle, the deoxygenated brine was placed in the chemostat. After adjusting its pH to 7.5 and temperature to 30°C, ethanol and bacteria culture were added at time zero. As soon as the nitrate was consumed in the batch cycle, the brine feed pump was turned on to provide oxygen-free brine at a specific dilution rate. After

reaching steady state at a particular dilution rate, the next dilution rate was applied. This procedure was continued until biomass washout occurred and the nitrate removal reached a steady value.

2.7. Pilot-Scale Rotating Biological Contactor (RBC) Experiments for Optimization

Laboratory-scale nitrification columns were not able to produce enough nitrified brine. The best alternative was to modify the existing RBC unit in the OCWD research area to produce sufficient quantity of nitrified solution to be used in the FBBR-GAC process. The following modifications were made: i) the top cover was removed to expose the reactor to the atmosphere in order to maintain aerobic conditions at all times, ii) a pH controller was added to monitor the pH changes, iii) two 55-gal collection containers were added to hold the nitrified brine, iv) a feed system was added to supply sodium thiosulfate and nutrients.

The RBC tank has 125-L capacity with three compartments, each holding one rotating disk made of polypropylene with a surface area of approximately $150 \text{ m}^2/\text{m}^3$. The RBC pilot studies involved the acclimation of nitrifying microorganisms, attachment of microorganisms onto the polypropylene support media, gradual increase in the influent flowrate to enhance good attachment and performance, and adopting preventative measures against slaughtering-off of the biomass formed. Furthermore, it was deemed necessary to add powdered activated carbon (PAC) to the system to enhance the nitrification process. Currently, the unit is capable of producing 100 ml/min of nitrified brine.

2.8. Laboratory-Scale FBBR-GAC Experiments

Several laboratory-scale FBBR-GAC experiments were conducted to investigate the effect of the GAC amount and detention time on the denitrification process efficiency. Initially, a synthetic brine concentrate was used in these studies due to the fact that the OCWD research RO unit faced operational problems and could not provide adequate amounts of brine solution. The nitrified influent brine was de-oxygenated with nitrogen gas to keep the dissolved oxygen level below 1%. The temperature was kept at 30°C by means of a water bath and the pH of the influent water was adjusted to 7.5 through the addition of acid and base. The denitrification column was charged with marble-size glass beads to about 3-in height in order to ensure uniform distribution of the influent. Subsequently, pre-cleaned and weighed GAC was charged into the column and the initial height was recorded. The GAC bed was then inoculated with acclimated denitrifying bacterial culture and placed in recycle mode for about half an hour. Finally, the feeding was

initiated at time zero and samples were taken at regular time intervals. Excess bacterial growth was removed from the column by stirring the GAC bed vigorously, and by scraping the column walls. The tubes to and from the column were cleaned periodically, and the excess pressure due to nitrogen gas generated by the bacterial reduction of nitrate was relieved when needed.

In the second phase of the GAC-FBBR experiments, real brine was used. Despite the numerous shut-downs of the research RO units, these experiments were conducted under the same environmental conditions as those with synthetic brine experiments.

2.9. Materials and Methods

2.9.1. Materials

2.9.1.1. Chemicals

Brine: Brine was collected in a 25-L polyethylene storage tank. When the RO unit was shut-down for maintenance or due to an operational failure, the brine was supplied from the main pilot plant's RO unit. The brine was provided from the main plant's RO unit in case of emergency.

Acid-Base: 0.1 N H_2SO_4 and 0.1 N NaOH were used for pH adjustment.

Carbon Source: The main carbon source is 100 percent purity ethanol.

Nutrients: Supplementary phosphate solution was added to ensure that phosphate was not the limiting nutrient.

Synthetic Brine Feed: It was necessary to prepare synthetic brine that did not include any nitrate for the nitrite limiting chemostat studies. The constituents of the synthetic brine are given in Table 2.1.

2.9.1.2. Bacterial Culture

A mixed microbial culture obtained from one of the anoxic tanks of a municipal wastewater treatment plant was used throughout this research. A mixed culture was preferred over a single strain culture for several reasons. Firstly, mixed cultures were more realistic in representing the actual denitrification process. Secondly, mixed cultures were readily available for use and easy to pre-acclimate since they were less sensitive to environmental conditions than single strain cultures. Lastly, literature reviews indicate that single cultures that work efficiently under laboratory conditions might fail under conditions encountered in a real process.

Table 2.1. Approximate concentrations of various constituents in the synthetically prepared nitrified brine concentrate

<u>Constituent</u>	<u>Represented by</u>	<u>Unit</u>	<u>Concentration</u>
TOC	Humic acid	mg/l	20
Total Dissolved Solids	NaCl	mg/l	4000
Organic N	Urea	mg/l	2
NH ₃ -N	(NH ₃) ₂ SO ₄	mg/l	10
NO ₃ -N	None	mg/l	-
NO ₂ -N	NaNO ₂	mg/l	150
SO ₄ ⁻²	CaSO ₄	mg/l	1150
Cl ⁻	NaCl	mg/l	1000
F ⁻	NaF	mg/l	1.5
Br ⁻	KBr	mg/l	1.7
PO ₄ ⁻³	Ca(H ₂ PO ₄) ₂	mg/l	20
HCO ₃ ⁻	KHCO ₃	mg/l	100
CN ⁻	KCN	μg/l	40
Ag	Ag ₂ SO ₄	μg/l	1.5
As	As ₂ O ₃	μg/l	14
Ba	BaCl ₂	μg/l	100
Cd	CdSO ₄	μg/l	1
Co	CoCl ₂	μg/l	2
Cu	CuCl ₂	μg/l	10
Fe	Fe ₂ (SO ₄) ₃	μg/l	300
Hg	Negligible	μg/l	-
Mn	MnSO ₄	μg/l	100
Pb	Pb(NO ₃) ₂	μg/l	2.5
Zn	ZnO	μg/l	60
Mg	MgSO ₄	mg/l	50
Ca	Ca(HCO ₃) ₂	mg/l	500

Initially, the deoxygenated brine concentrate stored in a 3-L borosilicate glass jar was inoculated with the microbial culture. Phosphate and ethanol were added, and the pH was adjusted to 7.0. Mixing was provided to ensure sufficient contact between the substrate and the microbial population. The growth of denitrifiers became abundant in a few days, and formed jelly-like agglomerated flocs. It was necessary to discard a portion of the culture every day in order to maintain the active microbial cells within the reactor. The presence of strong odor was evidence that sulfate reduction took place as soon as all the nitrates were consumed. The portion of bacterial culture utilized in the experiments was in lag or starvation phase as feeding was ceased two days prior to a new experiment.

2.9.1.3. GAC Characteristics

The type of GAC used in the research was coconut-shell-based activated carbon (COCL60) for water purification (Carbon Activated Corp., Los Angeles, CA). The specifications of the GAC were as follows:

Effective size:	8-12 US mesh
Particle Size:	1.5-2.0 mm (very uniformly distributed)
Apparent Density:	0.50-0.52 gm/cc
Specific Surface Area:	1100- 1150 m ² /gm
Hardness:	99.0% minimum
Moisture (as packed):	3.0% maximum
Bulk Density:	27.5 lb/ft

2.9.2. Analytical Methods

Ammonia, nitrate, nitrite, ethanol concentrations as well as pH and temperature of the influent and effluent brine were regularly monitored. All the procedures were in conformity with the methods described in Standard Methods (1995).

2.9.2.1. Analysis of Ammonia

A HACH Test Kit for Ammonia-Nitrogen with Nessler's Reagent (Loveland, Colorado) was used for the analysis of influent and effluent ammonia concentration. The influent brine was diluted 100 times to fall with the concentration range of the method.

2.9.2.2. Analysis of Nitrate, Nitrite and Sulfate

For the analysis of nitrate, nitrite, sulfate, fluoride and chloride, a DIONEX DX-100 One Column Ion Chromatograph with SRS Control (Sunnyvale, CA) equipped with a conductivity detector was used. The instrument had an automatic sampler, integrator, and a computer processor interface. The eluent was composed of a mixture of sodium carbonate and bicarbonate. Calibration was performed to check the analysis accuracy of the instrument. All samples were filtered through 0.22 μ cellulose acetate syringe filters. Samples with high TDS content were filtered through silver impregnated filters in order to reduce the chloride ion interference with the nitrite analysis. When it was not possible to immediately analyze the samples, they were stored in the refrigerator at 4°C until the time of analysis.

2.9.2.3. Analysis of Ethanol

A Perkin-Elmer Sigma 2B Gas Chromatograph (Norwalk, CT) was used to analyze for ethanol concentration in the samples. The chromatograph was equipped with a microprocessor based logic system capable of operating in either isothermal (150-450°C) or temperature programming mode. The chromatograph column was of Restek RTX-1 capillary type with dimensions of 60m length x 0.53 mm I.D. Hydrogen and helium were used as carrier gasses at 30 cc/min flowrate, and compressed air as combustion gas. The oven temperature was maintained at 80°C. A single flame ionization detector with temperature of 200°C was employed because of its high sensitivity to organic-containing compounds such as ethanol. The output was obtained from a data processor, integrator and data recorder. Duplicate samples were injected at an injector temperature value of 200°C manually using a syringe of 1 µl capacity, and the values were averaged.

2.9.2.4. Analysis of Mixed Liquor Volatile (Attached) Solids Concentration

The biomass obtained during the batch and chemostat tests were assayed according to Standard Methods (1995).

The biomass concentration for the batch and chemostat studies was assayed by the galvanimetric method described in Standard Methods (1995). The biomass for the FBBR-GAC column experiments was measured in terms of attached volatile solids (AVS) per gram of dry GAC. The alternative method would employ the procedure described by Hancher et al (1978). The bioparticles obtained from the reactor was washed with water in order to remove any non-attached biomass, and dried at 105°C for 24 hrs, cooled in the air and weighed. The bioparticles were then combusted at 550°C for 30 minutes, cooled and re-weighed. After washing the biomass-free particles with weak acid to remove its ash content, it was dried at 105°C for another 24 hrs, cooled and weighed. The difference in the weights gave the amount of attached biomass. The remaining GAC amount was weighed, and used in the calculation of biomass in terms of attached biomass per gram of dried GAC.

3. PROJECT OUTCOMES

3.1. Batch Experiments

Denitrification process is greatly influenced by temperature, pH, carbon to nitrogen (C:N) ratio and the salinity (total dissolved solids, TDS). Therefore, it is necessary to assess the effect of these parameters on the denitrification rate, and choose the optimum values.

3.1.1. Temperature Effect

A series of batch experiments covering a temperature range of 10-45°C were conducted to evaluate the effect of temperature on the denitrification rate. The specific denitrification rates obtained and presented in Table 3.1 were plotted against temperature in Figure 3.1 to get a clear picture of the temperature range in which the denitrification process proceeded efficiently.

Table 3.1. Batch denitrification results at different temperatures

	Temperatures (°C)							
	10	15	20	25	30	35	40	45
Time required for NO ₃ -N reduction (min)	535	360	275	275	125	95	85	190
NO ₃ -N concentration (mg/l)	72.02	62.07	72.44	65.73	59.59	52.51	53.09	58.11
Mid-time biomass concentration (mg/l)	591.84	492.86	382.98	272.11	357.89	317.90	372.36	551.35
Specific denitrification rate *	0.0137	0.0210	0.0413	0.0527	0.0799	0.1043	0.1006	0.0333
*(mg NO ₃ -N consumed/mg mid-time MLVSS.hr)								

As can be observed, the specific denitrification rate increased with temperature increase up to 35°C, underwent a slight decline at 40°C, followed by a sudden decline thereafter. As the temperature increased, the net amount of biomass produced during the experimental course decreased, while the specific denitrification rate increased. At temperatures 10, 15 and 45°C, the denitrification process took longer time than the process at the temperatures of 20, 25, 30, 35 and 40°C. At low temperatures, although the amount of biomass produced during the course of the experiment was higher, the denitrification activity was lower, which might imply suppression of

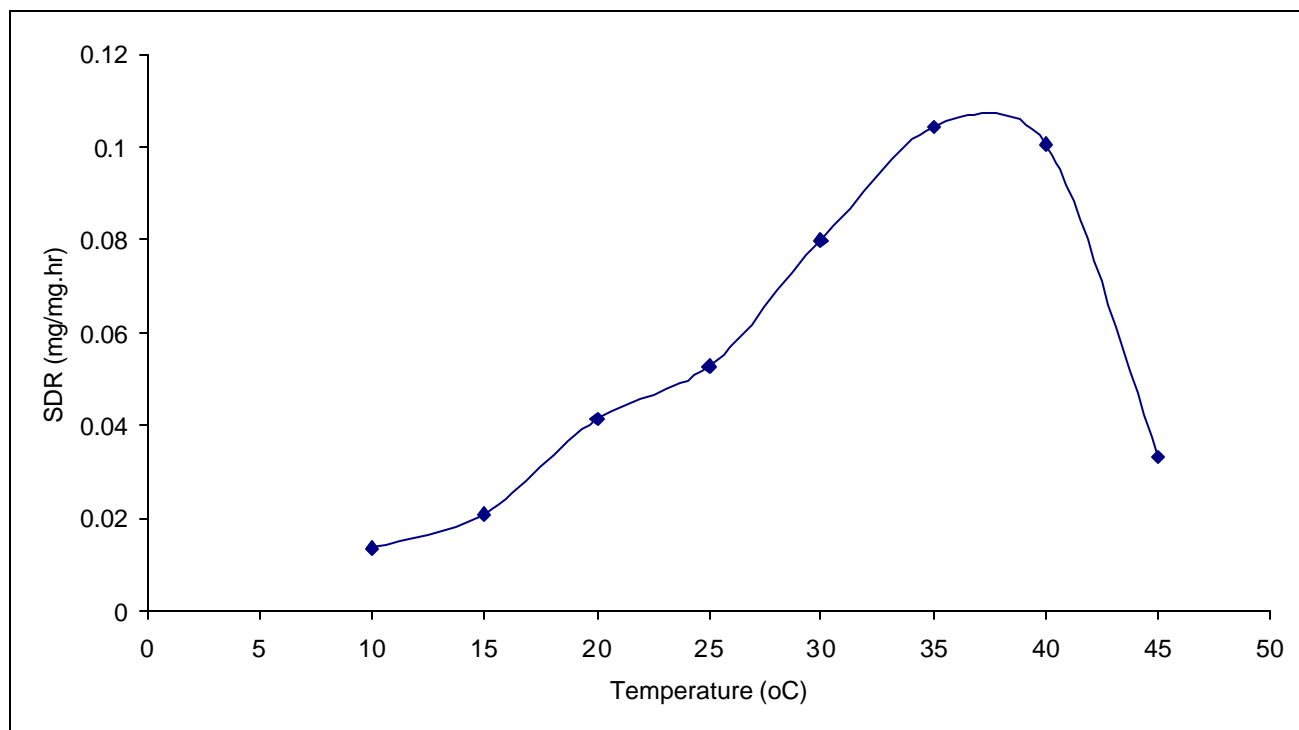


Figure 3.1. Effect of temperature on specific denitrification rate

bacterial enzyme activity or reductase production. Enzymatic activity or production of the reductases became more efficient as the temperature was increased to 45°C, although the biomass production was not as high as in lower temperatures since the experiments took less time for completion. At 45°C, the specific activity declined possibly due to the denaturation of bacterial enzymes. At all temperatures, nitrite accumulation was inevitable. In all temperature tests, nitrite removal did not begin to take place until almost all the nitrate was removed. This phenomenon seems to be in accord with the reported literature that states that nitrate is used preferentially over nitrite when there is no oxygen in the system, and when both nitrate and nitrite reductases present, resulting in accumulation of nitrite (Nakajima et al, 1984; Wilderer et al, 1987; Simpkin et al, 1988). Overall, the optimum temperature for the FBBR-GAC experiments was chosen as 30°C.

3.1.2. pH Effect

Another important parameter to be investigated was the pH. Denitrification reactions produce bicarbonate alkalinity, which caused an increase in the pH of the system. Any pH deviations from the optimal established value could impair the process unless pH control is provided. For this reason, a series of batch tests were conducted between the pH's 6 and 9 with increasing increments of 0.5.

The plot of specific denitrification rates (SDRs) shown in Table 3.2 vs. pH showed a bell-shaped curve with a peak around pH of 8 (Figure 3.2).

Table 3.2. Batch denitrification results at different pH

	6	6.5	7	pH 7.5	8	8.5	9
Time required for NO ₃ -N reduction (min)	230	175	165	125	100	125	165
NO ₃ -N concentration (mg/l)	58.62	57.83	64.25	59.59	58.11	64.13	59.21
Mid-time biomass concentration (mg/l)	393.50	400.00	371.90	357.89	432.20	432.43	427.27
Specific denitrification rate * *(mg NO ₃ -N consumed/mg mid-time MLVSS.hr)	0.0389	0.0496	0.0628	0.0799	0.0807	0.0712	0.0504

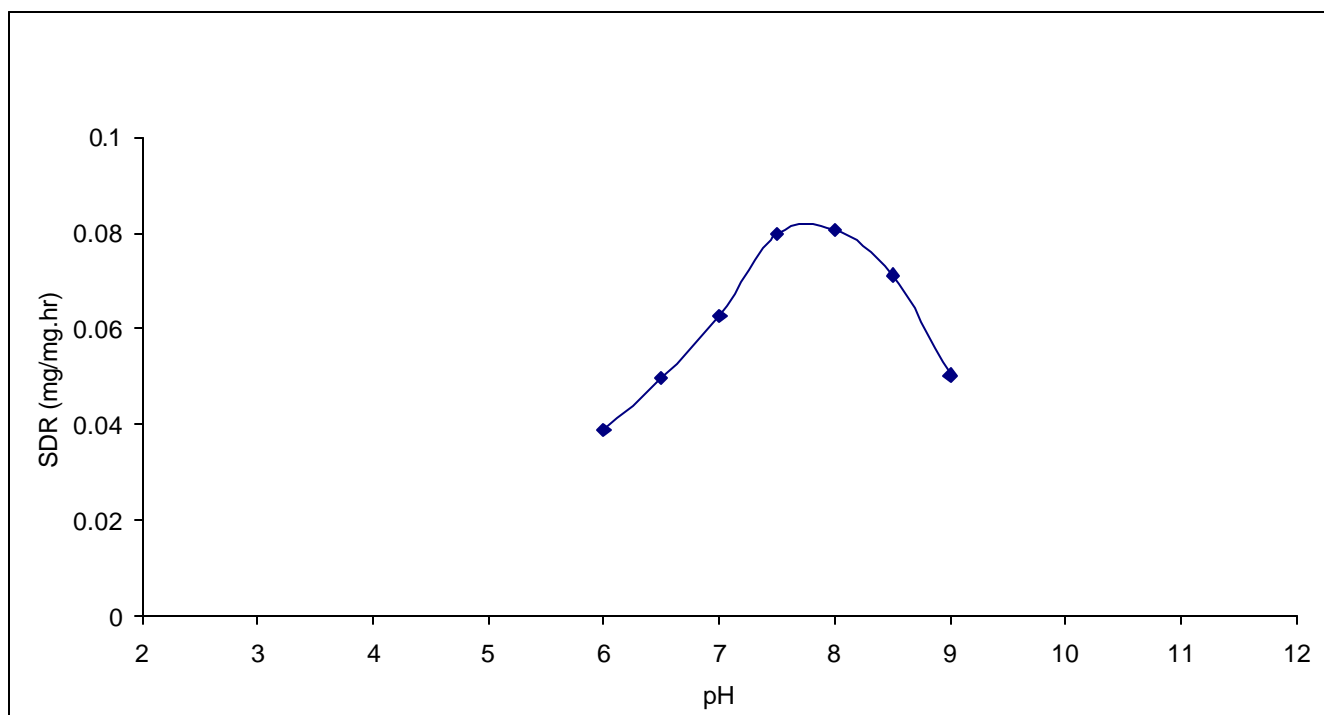


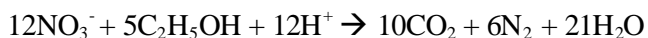
Figure 3.2. Effect of pH on specific denitrification rate

At lower pH values, especially at pH 6, denitrification still occurred, but completion took longer with significant amount of nitrite accumulation in the system. Accumulation continued to take place until almost all the nitrate was consumed. As soon as nitrate was consumed, nitrite reduction occurred, but at a slower rate. At pH values between 6.5 and 9, nitrate was consumed within or less than 2 hours. Nitrite accumulated in all experiments; however, as the pH increased, especially above 7.5, the accumulated nitrite concentration showed a substantial decline. This indicated that higher pH values favored faster nitrite or nitrate conversion with less accumulation of nitrite. At pH 9, the color of brine in the vessel became cloudy white, and formation of white flocs was observed. It is quite possible that a low buffering capacity might have led to the precipitation of the heavy metals from the brine concentrate. Lower pH values favored nitrate utilization vs. nitrite consumption. At pH's 8, 8.5 and 9, however, nitrite and nitrate consumption occurred simultaneously.

The batch run continued to observe the effect of high pH on the denitrification, as well as the effect of heavy metal precipitation on the biological process. The denitrification rate appeared to decline although nitrate removal was completed in a reasonably shorter period with less nitrite accumulation. The optimal pH value for the FBBR-GAC experiments was selected to be 7.5 (not 8.0) since there was a small difference in the specific denitrification rate between these two pH values.

3.1.3. Optimum Carbon-to-Nitrogen Ratio

The third parameter that has significance on the denitrification efficiency is the carbon to nitrogen ratio (C:N). The theoretical stoichiometric equation of denitrification with ethanol as the sole carbon source could be written as:



According to the stoichiometry, Constantin and Fick (1997) used a carbon to nitrogen ratio of 1.38 for practical purposes to cover the amount of ethanol that was required for biomass formation.

In order to achieve high denitrification rates with complete nitrate removal in a short time, a series of batch experiments were conducted on several carbon to nitrogen ratios (1.20:1, 1.52:1, 1.85:1 and 2.20:1) at 30°C temperature and pH value 7.5. Table 3.3 shows the calculated

specific denitrification rates and Figure 3.3 illustrates the change in specific denitrification rates with respect to the C:N ratios selected.

As evident from Figure 3.3, the optimal C:N ratio appeared to be between 1.52 and 1.85; 1.52 being the critical ratio. Below 1.85, the specific denitrification rate declined gradually. At C:N value of 1.52, the rate did not differ substantially from that at 1.85. Similarly, at C:N ratio of 2.2, the specific denitrification rate was very close to the corresponding value at 1.85. However, at the C:N ratio of 1.2, nitrite accumulated in the system, and although nitrate was totally consumed, nitrite reduction was incomplete. Significant amount of nitrite remained in the system, while no further reduction occurred, although the experiment was continued longer than anticipated. When higher C:N ratios were employed, the nitrite reduction occurred as expected; and the nitrate reductions were all complete. It can be observed from these results that the optimal C:N ratio lies somewhere between 1.52 and 1.85. Nevertheless, the ratio 1.85 is chosen to avoid the ethanol from becoming a limiting substrate, should the inflow nitrate concentration into the system fluctuate. This ratio would also provide for the amount of carbon utilized by the denitrifiers for cell formation.

Table 3.3. Batch denitrification results corresponding different Carbon-to-Nitrogen (C:N) ratios

	C:N (mg/mg)			
	1.2:1	1.50:1	1.85:1	2.2:1
Time required for NO ₃ -N reduction (min)	120	70	70	80
NO ₃ -N concentration (mg/l)	69.36	67.38	66.91	69.12
Mid-time biomass concentration (mg/l)	690.91	778.95	729.78	636.11
Specific denitrification rate* *(mg NO ₃ -N consumed/mg mid-time MLVSS.hr)	0.0502	0.0741	0.0786	0.0815

3.1.4. Effect of Total Dissolved Solids (TDS)

The effect of TDS on the denitrification efficiency was investigated. Salt concentrations above 1% (10,000 mg/l) were shown to inhibit the denitrification activity of denitrifying bacteria

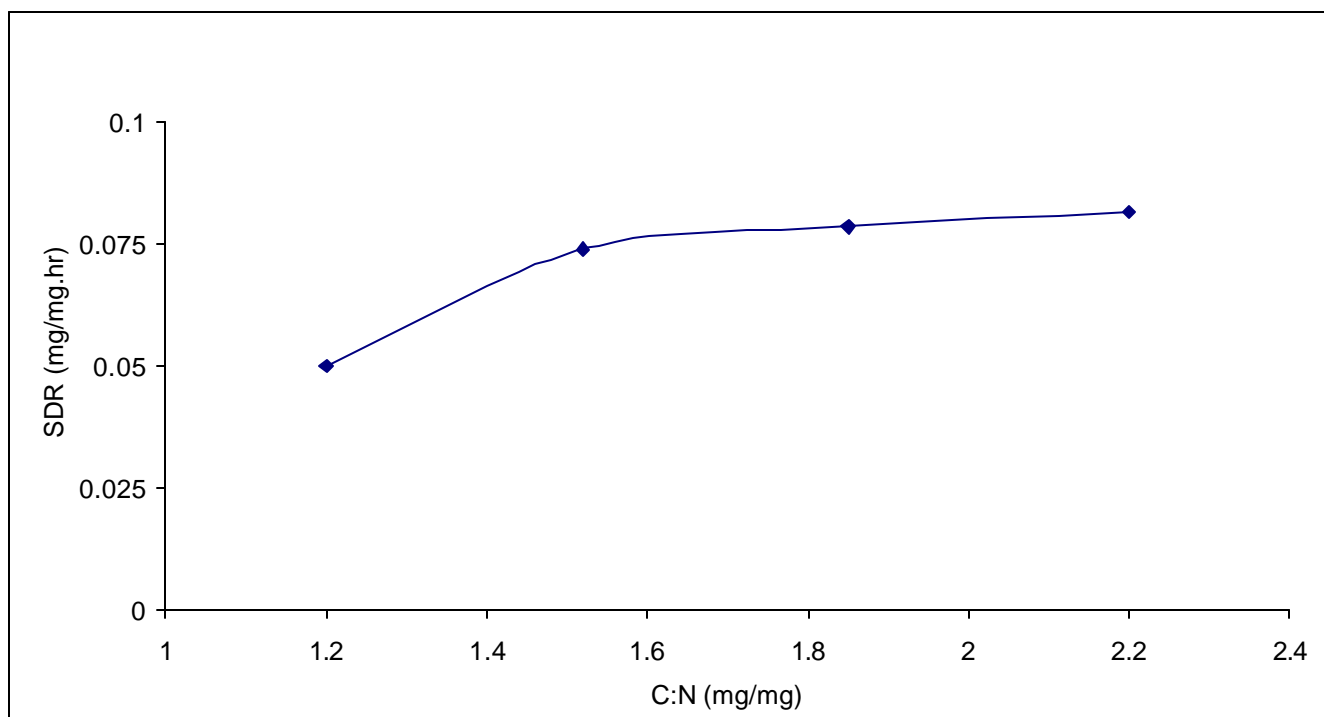


Figure 3.3. Effect of C:N ratio on specific denitrification rate

(Clifford and Liu, 1993). The reverse osmosis brine concentrate contained 4000 mg/l TDS on the average. Several batch tests were conducted to evaluate the effect of high salt concentrations on the denitrification efficiency of the system, considering the fact that there might be some fluctuations in the feed TDS concentration during normal operation. Three batch tests were carried out corresponding to TDS concentrations of 8000 mg/l (0.75%), 15,000 mg/l (1.45%) and 25,000 mg/l (2.4%), respectively, at 30°C temperature and pH of 7.5. Ethanol as the carbon source was not considered to be a limiting substrate in these experiments. Table 3.4 shows the computed denitrification rates and Figure 3.4 shows the variations in specific denitrification efficiency for different TDS values.

Table 3.4. Batch denitrification results for different total dissolved solid concentrations

	TDS (mg/l)			
	4000	8000	15000	25000
Time required for NO ₃ -N reduction (min)	125	90	90	100
NO ₃ -N concentration (mg/l)	59.59	65.41	57.00	57.71
Mid-time biomass	357.89	773.59	734.05	710.99
Specific denitrification rate*	0.0799	0.0564	0.0518	0.0487
*(mg NO ₃ -N consumed/mg mid-time MLVSS.hr)				

As evident from Figure 3.4, the denitrification activity dropped sharply from 0.0799 mg/mg.hr to 0.0564 mgNO₃-N/mg MLVSS.hr as the TDS concentrations were increased from 4000 to 8000 mg/l. As the TDS further increased, the denitrification activity also declined. In all cases, there was some nitrite accumulation which, interestingly, was consumed in a relatively short period of time. In the case of TDS concentration of 25,000 mg/l, the completion of nitrate reduction required longer time. In conclusion, the effect of high TDS concentration on the treatment activity was not as severe as anticipated. In fact, literature reported that pH, temperature and carbon to nitrogen ratio could have more significant impacts on the denitrification activity than the TDS concentration (Clifford and Liu, 1993). It is postulated that the fluctuations in the inflow TDS concentration would not significantly alter the denitrification efficiency of the system.

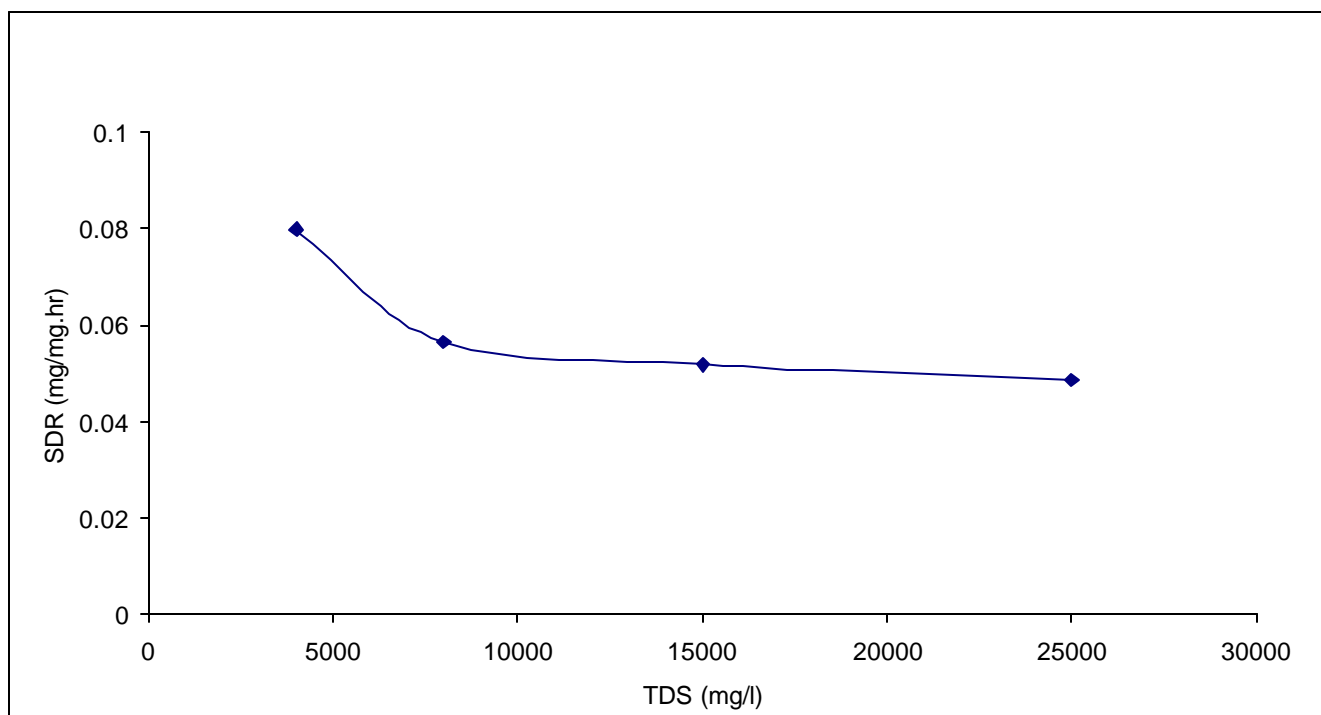


Figure 3.4. Effect of TDS concentration on specific denitrification rate

3.2. Chemostat Studies and Biokinetic Parameters

Kinetic constants are important parameters, which help evaluate the denitrification rate. They are determined through laboratory scale continuous chemostat tests. Continuous mode was preferred over batch because it simulates the real system more accurately.

A series of tests were conducted in completely mixed flow chemostat for determining the biological parameters pertaining to nitrate biodegradation. The nitrified brine concentrate was charged with microbial culture. The suspended culture was thoroughly mixed and purged with nitrogen gas to maintain anaerobic conditions. The temperature and pH was maintained at 30°C and 7.5, respectively. Samples were withdrawn periodically until a steady-state condition was reached with reference to nitrate concentration and biomass. After establishing steady-state condition, the flow rate to the reactor was incrementally increased in suitable step sizes, and the reactor operation was continued until a new steady state was reached. These steps were adopted repetitively for accurate determination of the biological parameters.

The experimental kinetic data could be used in a simple kinetic model which is based on the assumption that the denitrification occurred by consecutive reductions of nitrate to nitrite, and finally to nitrogen gas ($\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{Products}$). Furthermore, the assumption that reaction rates were limited by nitrate and/or nitrite concentrations was also important in the selection of a simple and effective model. The Monod kinetic model was selected for these investigations.

The generalized Monod model is:

$$m = \frac{\mu_m S}{K_s + S} \quad (3.1)$$

where

μ = Specific growth rate, hr^{-1}

μ_m = Maximum specific growth rate at saturation concentrations of growth limiting substrate, hr^{-1}

S = Residual growth limiting substrate concentration, mg/l

K_s = Saturation constant numerically equal to the substrate concentration at which $\mu = \mu_m/2$, mg/l

The rate equations corresponding to two-step denitrification model sequence can be expressed as follows:

$$\text{Cell growth: } \frac{dX}{dt} = \mu_{ma} \left(\frac{S_a X}{K_{sa} + S_a} \right) + \mu_{mb} \left(\frac{S_b X}{K_{sb} + S_b} \right) \quad (3.2)$$

$$\text{NO}_3\text{-N consumption: } \frac{dS_a}{dt} = - \frac{\mu_{ma} S_a X}{Y_a (K_{sa} + S_a)} \quad (3.3)$$

$$\text{NO}_2\text{-N consumption: } \frac{dS_b}{dt} = \frac{\mu_{ma} S_a X}{Y_a (K_{sa} + S_a)} - \frac{\mu_{mb} S_b X}{Y_b (K_{sb} + S_b)} \quad (3.4)$$

where:

X = Biomass concentration, mg/l

S_a = NO₃-N concentration, mg/l

S_b = NO₂-N concentration, mg/l

t = Reaction time, hr

μ_{ma} = Maximum specific growth rate for the biomass consuming NO₃-N, hr⁻¹

μ_{mb} = Maximum specific growth rate for the biomass consuming NO₂-N, hr⁻¹

K_{sa} = Half saturation constant for NO₃-N reduction, mg/l

K_{sb} = Half saturation constant for NO₂-N reduction, mg/l

Y_a = Growth yield coefficient for the biomass consuming NO₃-N, mg MLVSS produced/mg NO₃-N utilized

Y_b = Growth yield coefficient for the biomass consuming NO₂-N, mg MLVSS produced/mg NO₂-N utilized

μ = Overall specific growth rate (NO₃-N + NO₂-N), hr⁻¹

μ_m = Overall maximum specific growth rate (NO₃-N + NO₂-N), hr⁻¹

In the chemostat studies, the temperature was maintained at 30°C and the pH at 7.5. Mixing was provided at 400 rpm at all times. The dissolved oxygen concentration was kept at nearly zero to promote anaerobic conditions (nitrogen gas was used to deoxygenate both the chemostat and the feed water).

Two continuous chemostat tests were carried out:

1. Nitrite limiting chemostat (ethanol in excess)
2. Nitrate limiting chemostat (ethanol in excess)

3.2.1. Nitrite-Limiting Chemostat

The nitrite limiting chemostat test employed synthetic brine containing 163 mg/l NO₂-N, 500 mg/l ethanol, but no nitrate. The initial feed flowrate was 2 ml/min, and the biomass washout occurred at a flow rate of 15 ml/min. Nitrite accumulation was observed only in the initial batch stage of the experiment before the feeding was started, and close to washout, but not in-between these periods. Nitrite began to accumulate at the flowrate of 8.75 ml/min, and its concentration in the chemostat kept increasing until the total washout occurred. At a flow rate of 15 ml/min, most of the biomass and ethanol were washed out from the fermentor, and only small amount of nitrite reduction was observed. Table 3.5 shows the overall results of nitrite-limiting chemostat, and Figure 3.5 shows the variations in nitrite, ethanol and biomass concentrations with respect to time.

The biomass yield per unit mass of substrate (nitrogen or ethanol), Y_b, is determined from the plot of the specific substrate utilization rate (SDR_b) versus the specific growth rate (μ_b) according to the formula:

$$SDR_b = \frac{1}{Y_b} m_b + k_d \quad (3.5)$$

where

SDR_b = specific substrate utilization rate, mg NO₂-N/mg biomass.hr

k_d = specific substrate utilization rate for energy and maintenance, hr⁻¹

Table 3.5. Overall results for nitrite limiting chemostat

Time (min)	u=D (hr ⁻¹)	NO ₂ -N conc. (mg/l)	EtOH conc. (mg/l)	X _{avg} (mg MLVSS/l)	SDR (NO ₂ -N) (mg N/mg X)	SDR (EtOH) (mg Et/mg X)
95	0.089	162.99	300.77	452.22	0.228	0.42
100	0.133	162.99	373.69	400	0.245	0.561
90	0.178	162.99	405.83	356.05	0.305	0.76
90	0.267	162.99	415.01	352.2	0.309	0.786
75	0.389	153.07	400.49	294.33	0.416	1.089
60	0.578	101.32	333.78	226.46	0.447	1.474
55	0.622	73.12	292.29	161.18	0.495	1.978
35	0.667	29.46	125.25	94.59	0.515	2.27

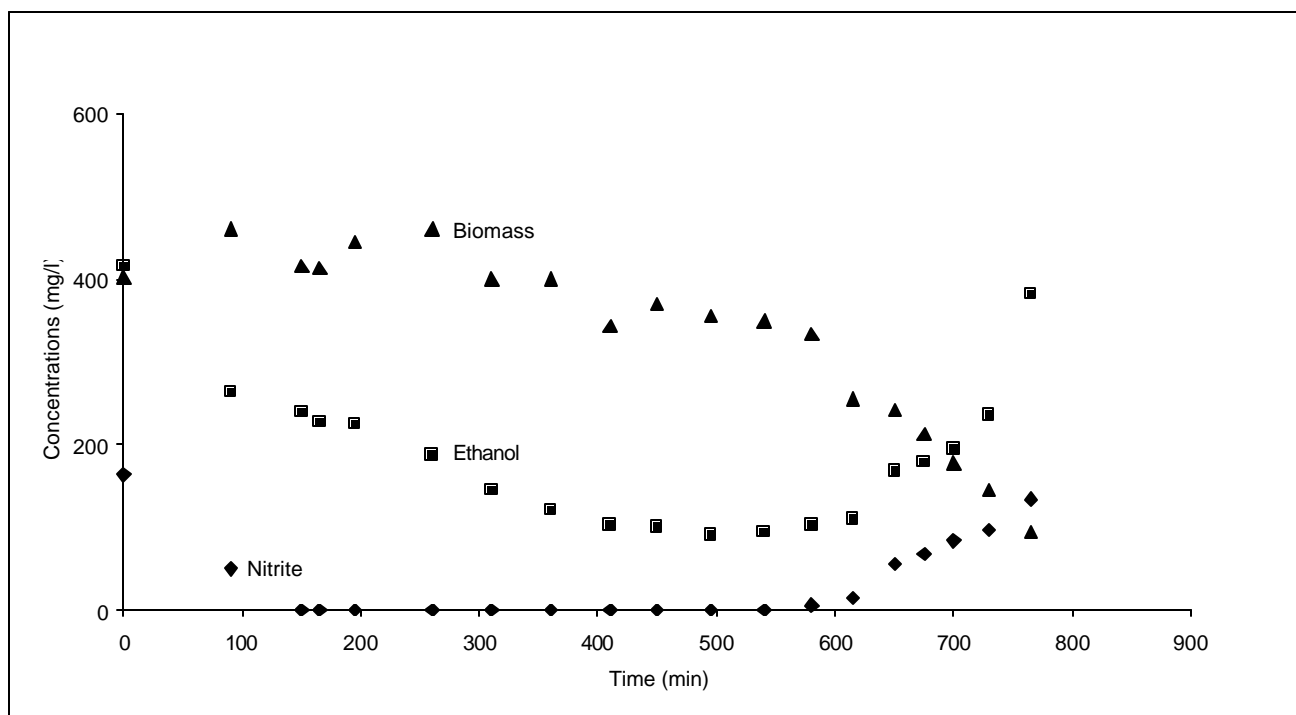


Figure 3.5. Variation of nitrite, biomass and ethanol concentrations with respect to time in nitrite-limiting chemostat

The plots of $\text{SDR}_{\text{NO}_2\text{-N}}$ vs. μ_b and SDR_{EtOH} vs. μ_b are shown in Figure 3.6. The reciprocals of slopes of these lines provide the growth yield with respect to nitrite utilization ($Y_{\text{NO}_2\text{-N}}$), and the growth yield with respect to ethanol utilization (Y_{EtOH}) as **2.10** and **0.35**, respectively.

The Monod equation is converted to the following form to estimate the Monod maximum specific growth rate, μ_{mb} , and half saturation constant, K_{sb} . The inverse of the intercept gives the former, while the latter is found by multiplying the value of μ_m by the slope.

$$\mu_b = \frac{\mu_{mb} S_b}{K_{sb} + S_b} \quad (3.6)$$

The above equation is written in reciprocal form as:

$$\frac{1}{\mu_b} = \frac{1}{\mu_{mb}} + \frac{K_{sb}}{\mu_{mb}} \frac{1}{S_b} \quad (3.7)$$

As seen from the Lineweaver-Burke plot shown in Figure 3.7, the maximum specific growth rate, μ_{mb} is equal to **0.675 hr⁻¹**, and the half saturation constant K_{sb} is equal to **7.30 mg/l**.

3.2.2. Nitrate-Limiting Chemostat

Nitrate limiting chemostat contained 75.6 mg/l $\text{NO}_3\text{-N}$, 1000 mg/l ethanol and no nitrite initially. As soon as the nitrate concentration dropped to 0 mg/l in the batch stage, during which no brine was fed into the chemostat, the brine feeding commenced. The initial feed flowrate was 2 ml/min, and the washout occurred at a flowrate of 17 ml/min. Nitrite accumulation was observed only in the initial batch stage, and close to washout, but not in-between these periods. Shimuzu et al (1978) operated continuous chemostats under steady-state conditions, and reported that nitrite did not accumulate in significant amounts even at higher dilution rates in their systems. The possible reasons reported were: (i) nitrite could be washed out of the reactor, and (ii) the saturation constant for reduction was much lower than that for nitrate reduction. Nitrate began to accumulate at the flowrate of 9 ml/min, and its concentration progressively increased until washout occurred. At a flowrate of 17 ml/min, most of the biomass and ethanol were already washed out, and there were undetectable levels of nitrite reduction. The specific denitrification rates are shown in Table 3.6. The variations in nitrate, nitrite, ethanol and biomass concentrations with respect to time are presented in Figure 3.8.

Table 3.6. Overall result for nitrate limiting chemostat

Time (min)	$\mu=D$ (hr ⁻¹)	NO ₃ -N conc. (mg/l)	EtOH conc. (mg/l)	X_{avg} (mg MLVSS/l)	SDR (NO ₃ -N) (mg N/mg X)	SDR (EtOH) (mg Et/mg X)
60	0.089	75.61	358.62	476.62	0.159	0.75
60	0.111	76.23	354.6	440.42	0.173	0.81
60	0.133	76.23	354.95	406.87	0.187	0.87
60	0.178	76.23	463.67	397.91	0.192	1.17
60	0.222	76.23	561.1	370.68	0.206	1.51
60	0.267	76.23	662.41	365.78	0.209	1.81
60	0.4	75.75	677.71	327.44	0.234	2.07
55	0.533	66.48	490.05	240.48	0.301	2.22
45	0.622	45.5	293.44	179.31	0.309	2.18
35	0.711	24	184.97	116.41	0.324	2.28
30	0.756	13.86	74.55	68.97	0.345	2.16

The biomass growth yields per unit mass of nitrate and ethanol utilized, Y_{NO_3-N} and Y_{EtOH} , respectively, could be determined from the chemostat data by plotting the specific substrate utilization rates (SDR_a) vs. specific growth rate (μ_a):

$$SDR_a = \frac{1}{Y_a} \mu_a + k_d \quad (3.8)$$

where

SDR_a = Specific substrate utilization rate, mg Substrate/mg MLVSS.hr

k_d = Specific substrate utilization rate for energy and maintenance, hr⁻¹

The plots of SDR_{NO_3-N} versus μ and SDR_{EtOH} versus μ are shown in Figure 3.9. The reciprocal of slopes of these lines provides the estimates of the growth yield with respect to nitrate utilization (Y_{NO_3-N}) and the growth yield with respect to ethanol utilization (Y_{EtOH}) as **3.78** and **0.45**, respectively.

The following differential equation could be derived by applying the kinetic equations (7.2), (7.3) and (7.4) to the mass balance relation. Then, the Monod equation could be converted into the following form to calculate maximum specific growth rate, μ_{ma} and half saturation constant K_{sa} .

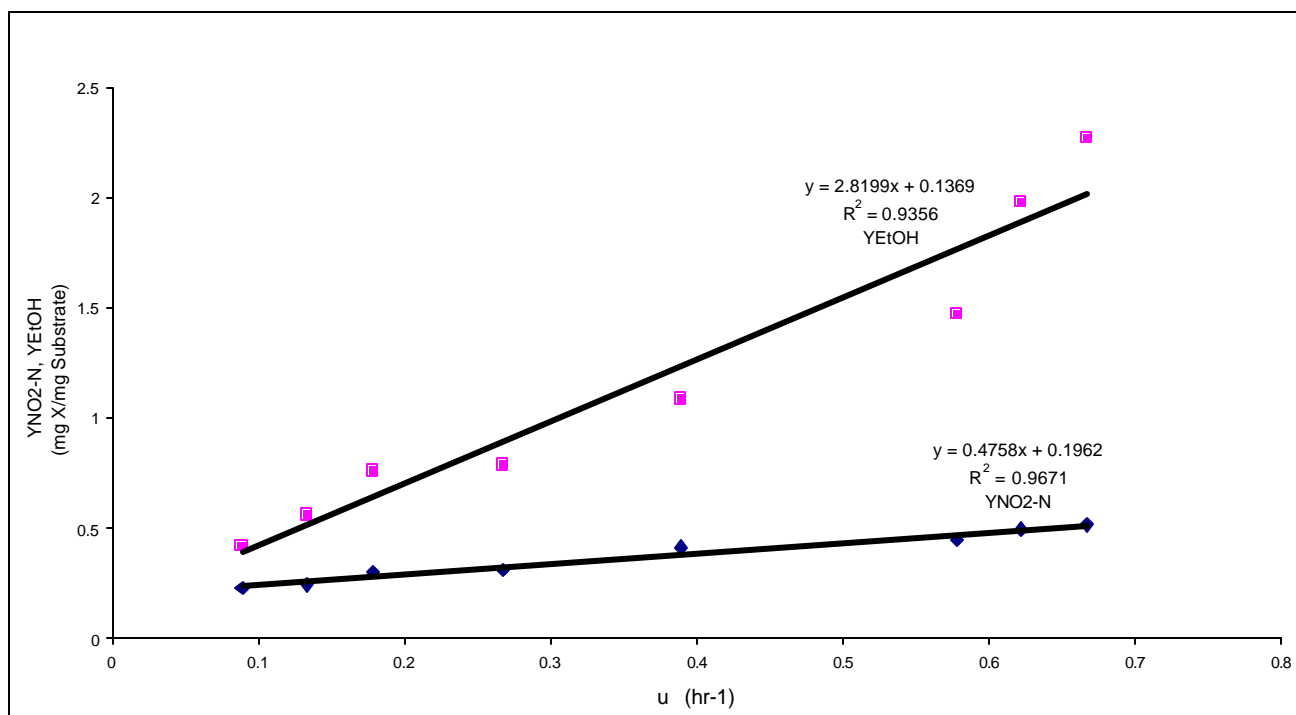


Figure 3.6. Graph for yield coefficients in nitrite-limiting chemostat

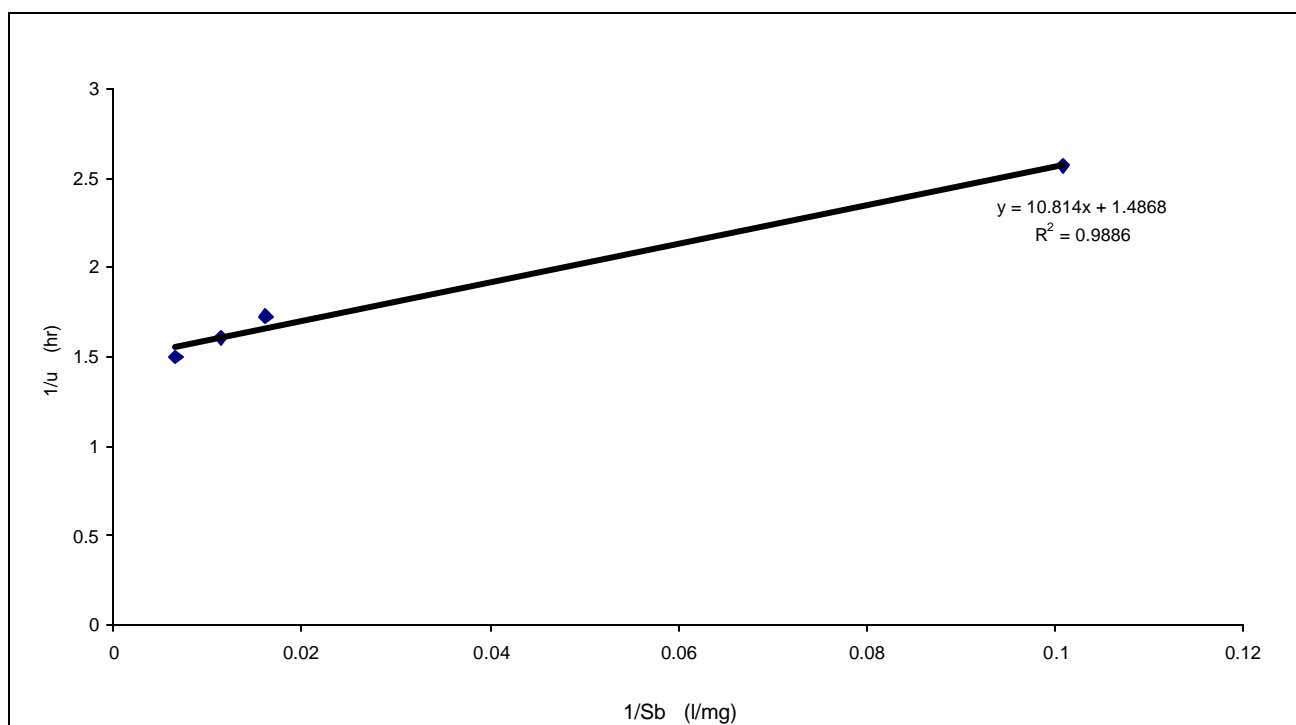


Figure 3.7. Plot for kinetic coefficients in nitrite-limiting chemostat

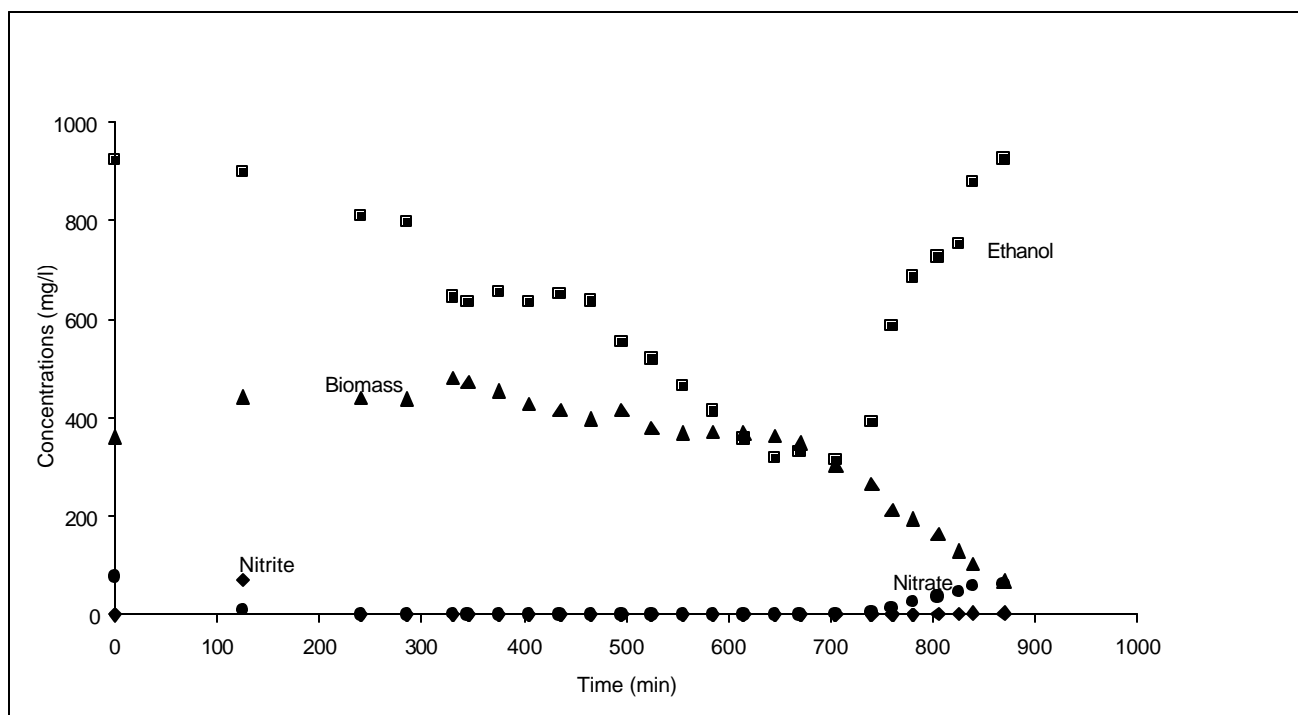


Figure 3.8. Variation of nitrate, nitrite, biomass and ethanol concentrations with respect to time in nitrate-limiting chemostat

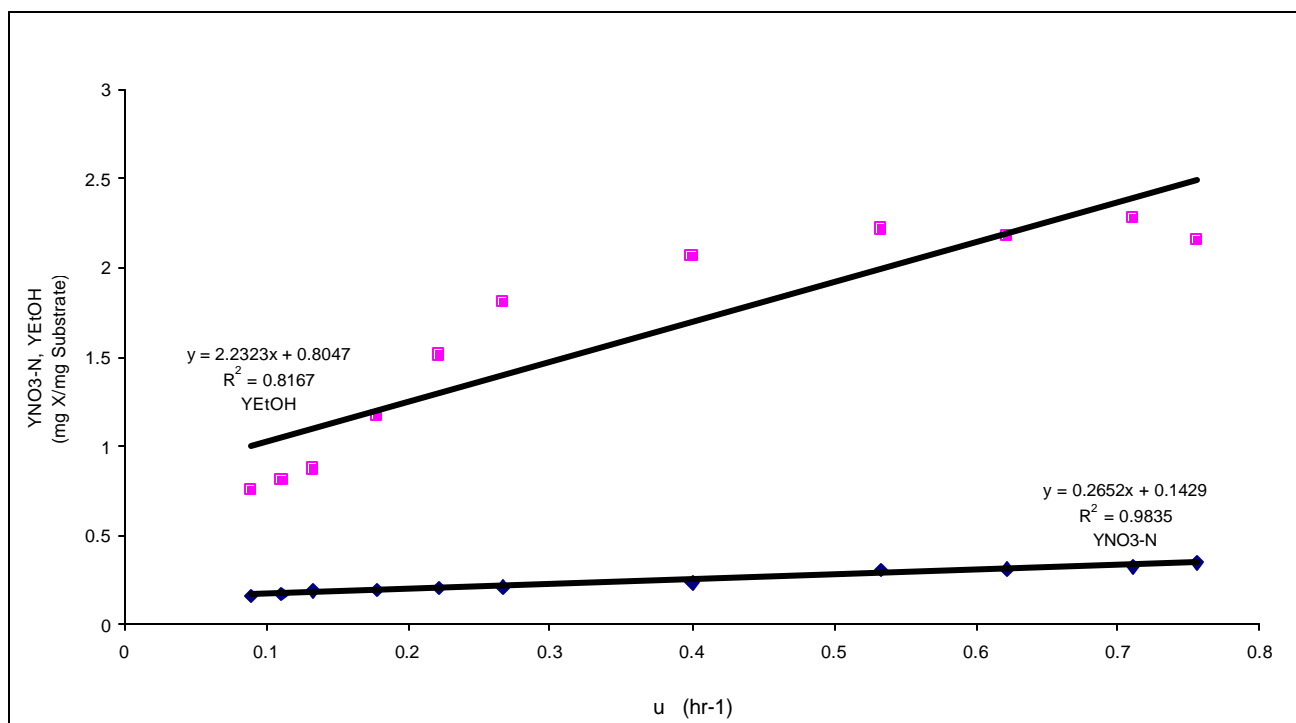


Figure 3.9. Graph for yield coefficients in nitrate-limiting chemostat

The reciprocal of the intercept gives the former while the latter is found by multiplying the value of μ_{ma} by the slope.

$$\frac{dX}{dt} = -DX + \frac{m_{ma}S_aX}{K_{sa} + S_a} + \frac{m_{mb}S_bX}{K_{sb} + S_b} \quad (3.9)$$

where D = Dilution rate, hr^{-1}

Under steady state conditions, dX/dt is equal to 0, and the dilution rate equals the specific growth rate so that D can be replaced by μ .

$$-\mu X + \frac{m_{ma}S_aX}{K_{sa} + S_a} + \frac{m_{mb}S_bX}{K_{sb} + S_b} = 0 \quad (7.10)$$

Rearranging the above equation would give:

$$\mu X - \frac{m_{ma}S_aX}{K_{sa} + S_a} = \frac{m_{mb}S_bX}{K_{sb} + S_b} \quad (3.11)$$

After dividing both sides by X , and then taking the reciprocal, we obtain:

$$\frac{1}{\left[\mu - \frac{m_{ma}S_a}{K_{sa} + S_a} \right]} = \frac{K_{sa}}{m_{ma}S_a} + \frac{1}{m_{ma}} \quad (3.12)$$

Substituting the values of μ_{nb} and K_{sb} , obtained from the $\text{NO}_2\text{-N}$ limiting chemostat into the above equation, a plot of $(1/(\mu - (\mu_{nb}S_b/K_{sb} + S_b)))$ vs. $1/S_a$ was prepared. This plot yielded μ_{ma} from the intercept value, and K_{sa} from the slope value (Lineweaver-Burke plot in Figure 3.10). These parameters were estimated to be μ_{ma} **0.675** hr^{-1} and K_{sa} **27.49** mg/l .

At higher dilution rates, it can be postulated that $S_a > K_{sa}$ and $S_b > K_{sb}$ so that the overall maximum specific growth rate for $\text{NO}_3\text{-N}$ limiting step can be represented as the sum of maximum substrate utilization rates μ_{ma} and μ_{mb} as shown below:

$$m_m = m_{ma} + m_{mb} \quad (3.13)$$

so that:

$$m_{ma} = 0.675 + 0.675 = \mathbf{1.35 \text{ hr}^{-1}}$$

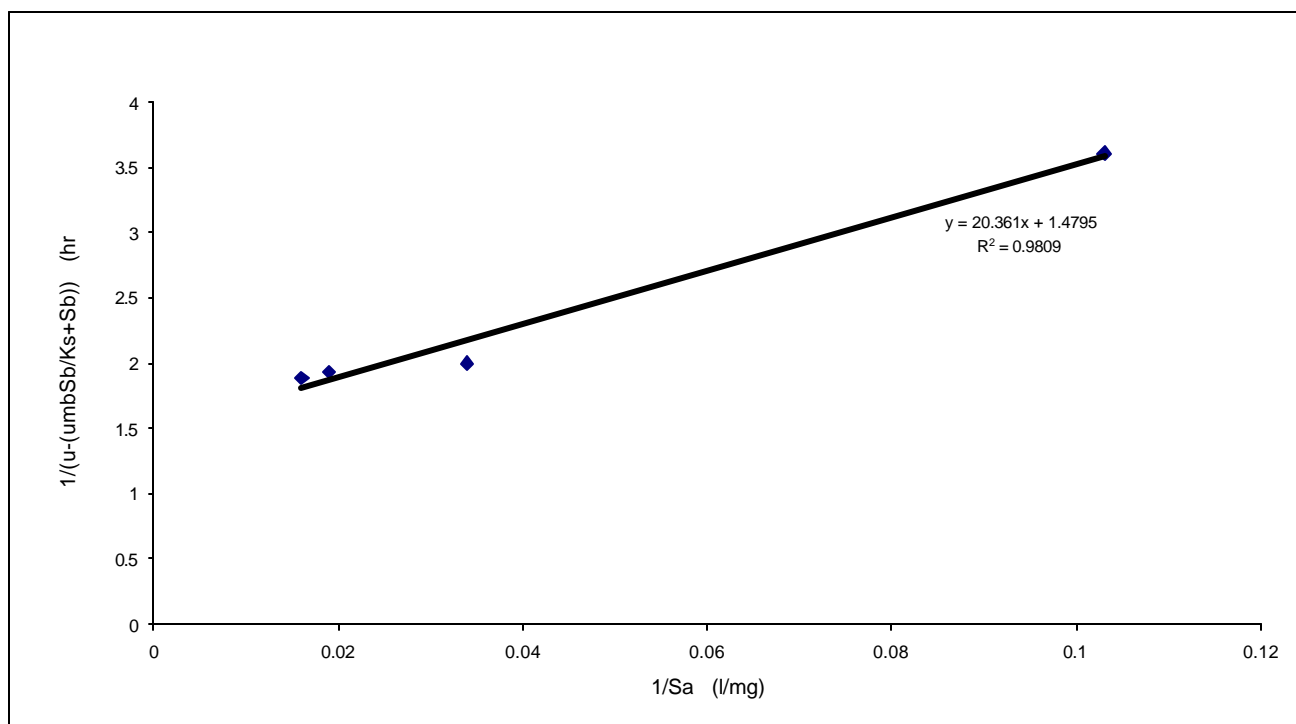


Figure 3.10. Plot for kinetic coefficients in nitrate-limiting chemostat

The maximum specific growth rate in the nitrate-limiting chemostat is twice that of the nitrite-limiting chemostat, and the half saturation constant for the nitrite reduction is about one-fourth of that for nitrate reduction. This, according to Shimizu et al (1978), could suggest that in the nitrite reduction process, the production of biomass, the consumption of energy and carbon source per unit mass of nitrogen removed would be lower than in the nitrate reduction process. Moreover a lower effluent nitrate concentration could be obtained in the nitrite denitrifying systems. The growth yields based on nitrate utilization are much larger than that of obtained by ethanol utilization. This was expected because nitrate is the limiting substrate as we assumed in the beginning of the chemostat studies.

The biokinetic parameters, μ_m (maximum specific growth rate), K_s (half saturation constant), Y (yield coefficient), and k_d (decay constant) determined from the results of these continuous culture chemostat experiments are tabulated below in Table 3.7.

Table 3.7. Kinetic constants for denitrification of brine

	μ_m (hr ⁻¹)	K_s (mg/l)	Y_N	Y_{EtOH}	k_d (hr ⁻¹)
Nitrate limiting chemostat (excess ethanol)	1.35	27.49	3.78	0.45	0.54
Nitrite limiting chemostat (excess ethanol)	0.675	7.30	2.10	0.35	0.412

3.3. Laboratory Scale FBBR-GAC Studies

As mentioned before, two series of laboratory scale FBBR-GAC experiments were conducted. The first series used synthetic nitrified brine that had the same constituents as the brine used in the limited chemostat studies, and the second series employed the actual nitrified brine obtained from the Rotating Biological Contactor system. In all these experiments, different amounts of GAC were used with varying hydraulic retention times and influent nitrate concentrations.

Initially, the denitrification column was charged with marble-size glass beads to a height of 3 in. to ensure uniform distribution of the influent. Subsequently, pre-washed and weighed GAC was charged into the column and the initial height was recorded. The GAC bed was then

inoculated with the acclimated microbial culture and placed in recycle mode for about half an hour. Finally, the feeding was initiated at time zero. The feed was continuously purged with nitrogen gas to maintain anaerobic conditions. The influent to the column was fed with ethanol at a C:N ratio of about 1.85:1 by weight, and the pH and temperature were maintained at 7.5 and 30°C, respectively. It is important to note that the values for the C:N ratio, temperature, pH were obtained from the optimized batch experiments discussed in section 3.2. A portion of the fluid in the adsorber column was recycled to maintain the fluidization of the adsorber bed, and the final bed height was recorded. The samples from these experiments were collected at regular time intervals, passed through 0.2 μ syringe filters, and refrigerated until the time of analysis. Biomass growth in the column caused the GAC bed to expand. The excess biomass growth on the GAC particles was periodically removed by vigorously mixing the adsorber bed for a few minutes. The GAC particles that became less dense due to biomass growth were consequently washed out in the recycle flow, and were collected at the bottom cone-section of the column and returned to the GAC bed. The biomass analysis was performed on a pre-determined quantity of GAC removed from the bed at the end of each experimental run.

In the present investigation, eight sets of experiments were carried out with synthetic brine. Three experimental runs were conducted using 300 g of GAC and approximately 400 mg/l of initial nitrate concentration with different hydraulic retention times of 60, 120 and 180 minutes. In all three cases, the denitrification was complete as shown in Figures 3.11, 3.12, and 3.13. Similarly, three sets of experiments were conducted with 150 g of GAC using the same hydraulic retention times and initial nitrate concentrations. All three experiments achieved full denitrification as shown in Figures 3.14, 3.15, and 3.16. The last two sets of experimental runs employed a much higher nitrate concentration of about 1300 mg/l. Again, complete denitrification was achieved as evident from the results presented in Figures 3.17 and 3.18. At shorter hydraulic retention times, the denitrification process required a longer time for completion with significant nitrite accumulation. After reaching the peak, nitrite concentration was slowly reduced along with nitrate, and when nitrate concentration stabilized, no nitrite accumulation occurred. On the other hand, nitrite accumulation considerably decreased with lower amounts of GAC. Even when the initial nitrate concentration was tripled, almost the same amount of time was required for the system to reach steady state. The nitrite accumulation was significantly higher in the column with 300 g of GAC than in the column with only 150 g.

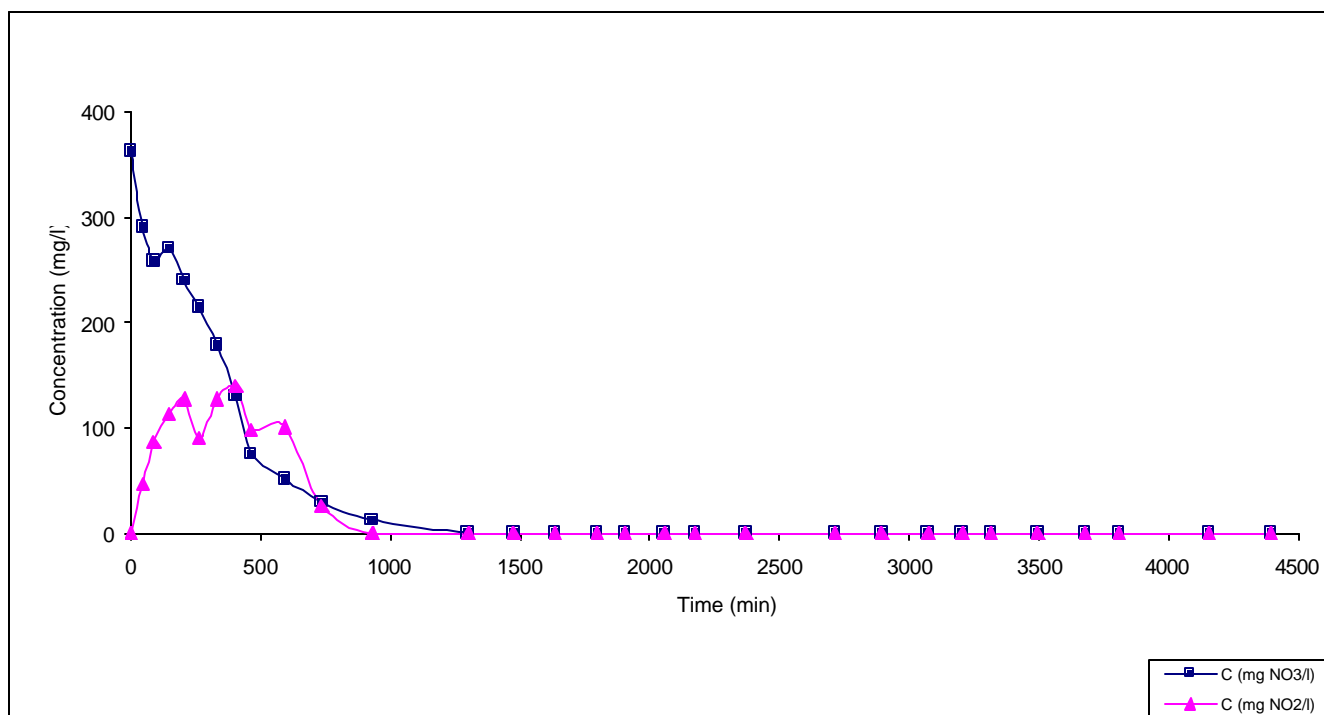


Figure 3.11. FBBR-GAC denitrification efficiency (Carbon=300 g, Flowrate=28.5 ml/min, HRT=60 min)

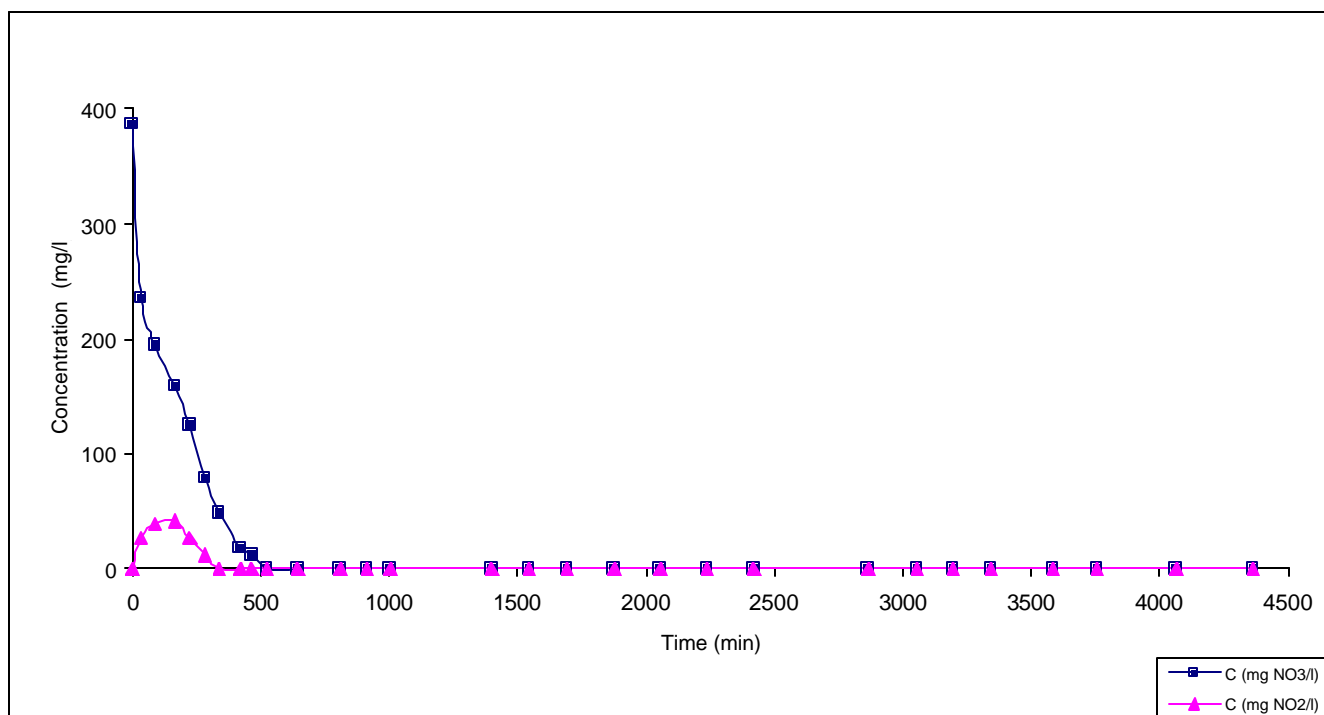


Figure 3.12. FBBR-GAC denitrification efficiency (Carbon=300 g, Flowrate=14.3 ml/min, HRT=120 min)

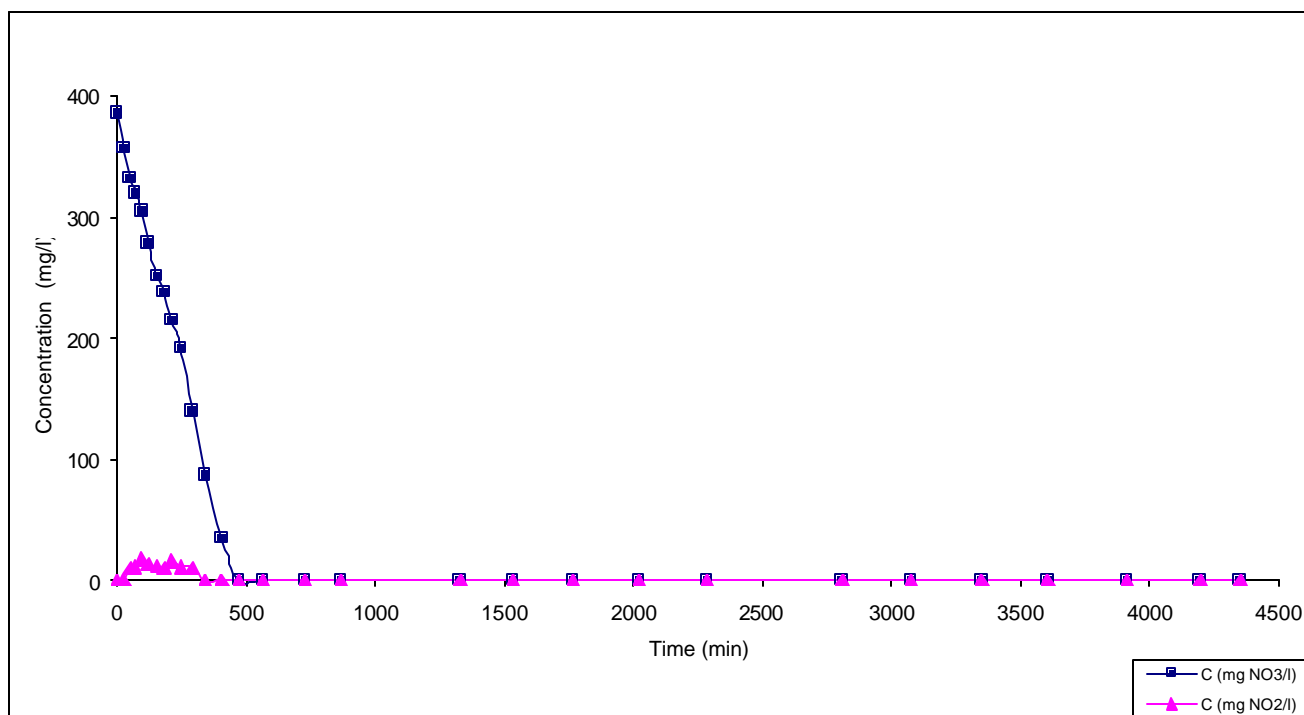


Figure 3.13. FBBR-GAC denitrification efficiency (Carbon=300 g, Flowrate=9.5 ml/min, HRT=180 min)

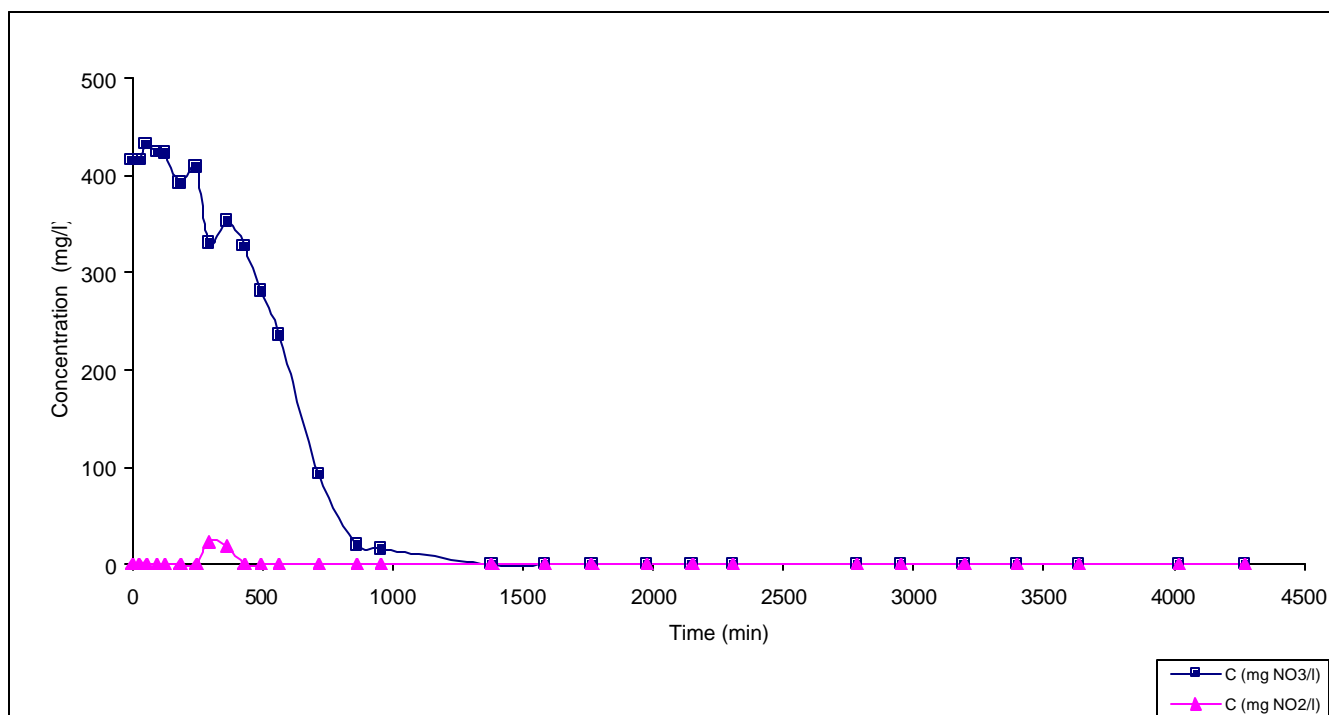


Figure 3.14. FBBR-GAC denitrification efficiency (Carbon=150 g, Flowrate=28.5 ml/min, HRT=60 min)

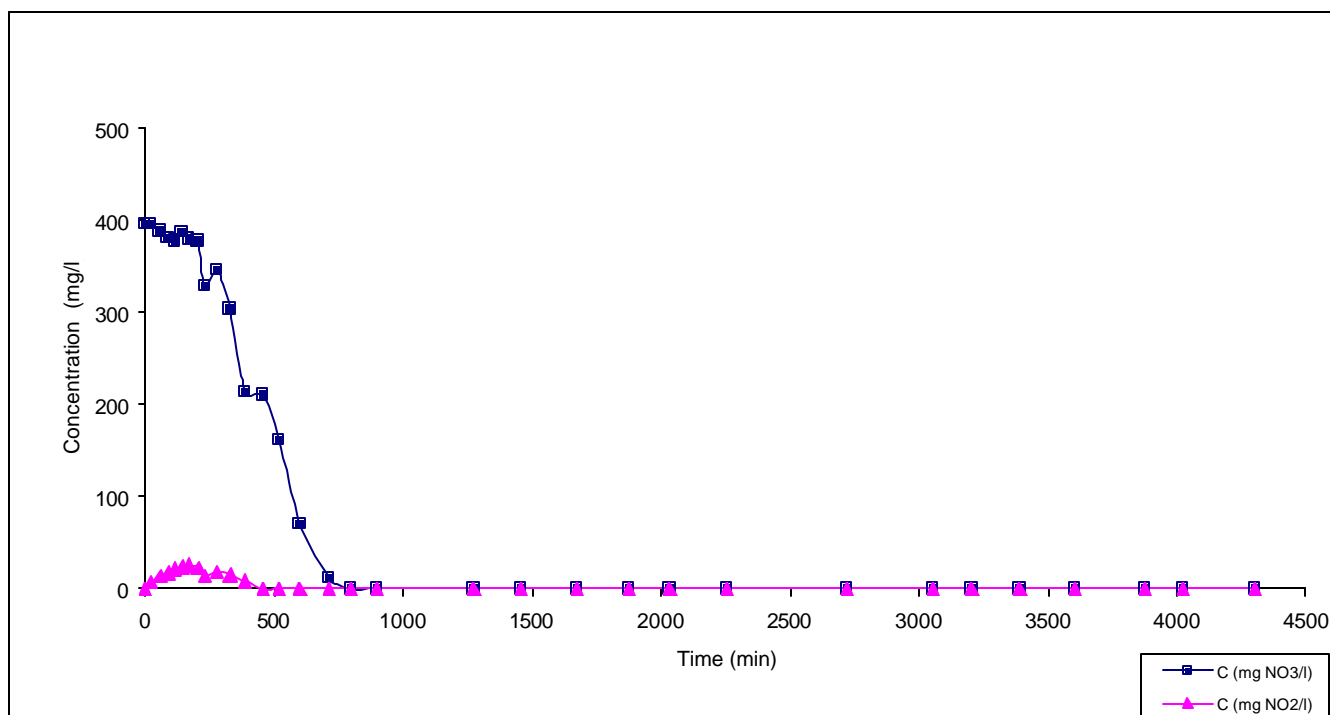


Figure 3.15. FBBR-GAC denitrification efficiency (Carbon=150 g, Flowrate=14.3 ml/min, HRT=120 min)

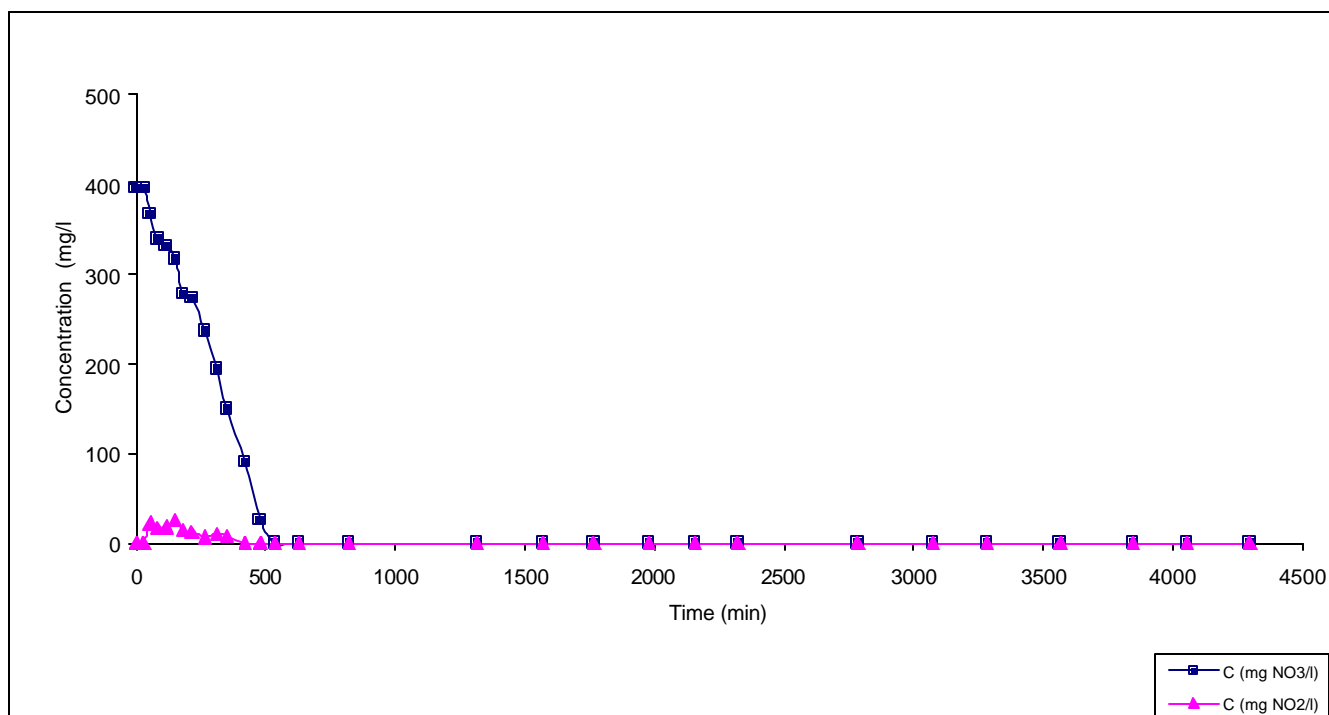


Figure 3.16. FBBR-GAC denitrification efficiency (Carbon=150 g, Flowrate=9.5 ml/min, HRT=180 min)

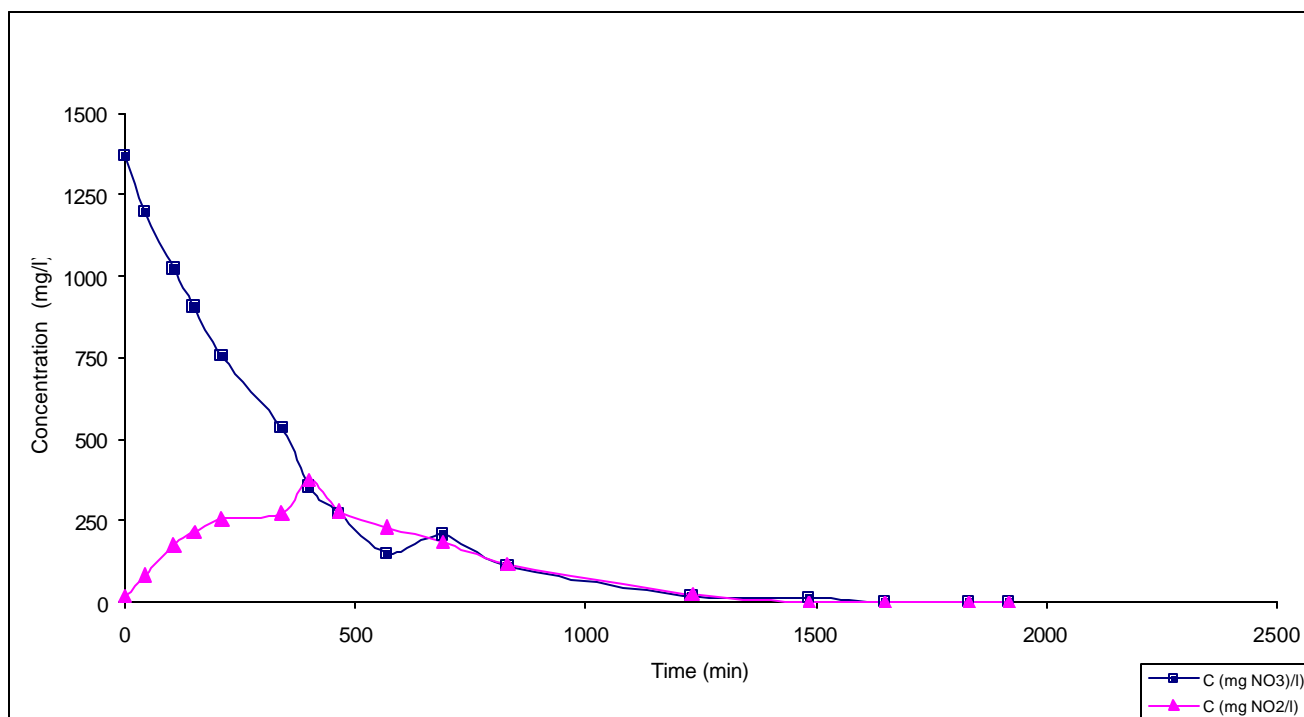


Figure 3.17. FBBR-GAC denitrification efficiency (Carbon=150 g, Flowrate=19 ml/min, HRT=90 min)

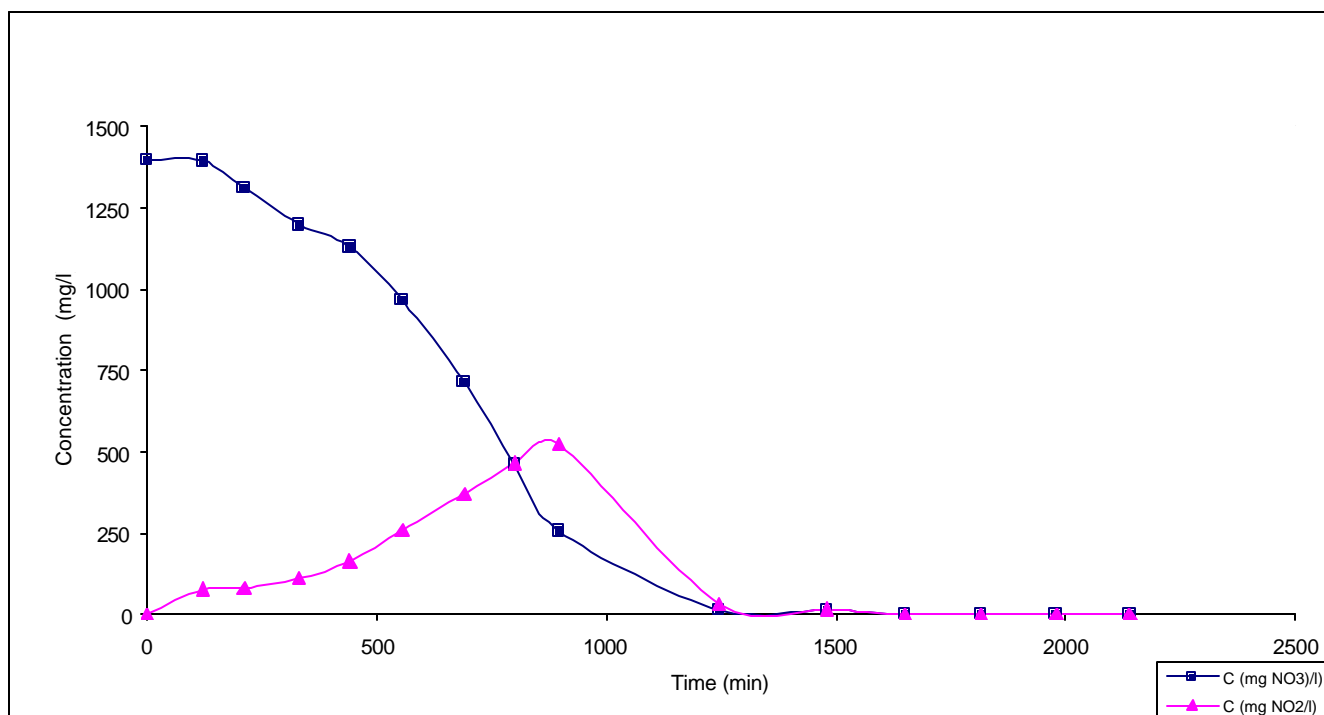


Figure 3.18. FBBR-GAC denitrification efficiency (Carbon=300 g, Flowrate=19 ml/min, HRT=90 min)

The second set of experiments employed actual nitrified brine. The first three series of experimental runs employed nitrate concentration of 800 mg/l. Of these, two experimental runs employed 150 g and 300 g of GAC with a hydraulic retention time of 56 minutes, and their removal efficiencies were 98.4% and 97%, respectively, as presented in Figures 3.19 and 3.20. Nitrite accumulation was higher in the column employing 300 g of GAC than in that employing 150 g GAC. However, in both columns nitrite reduction was complete after nitrate concentration was reduced, and no further nitrite accumulation was detected. The experiment which was conducted with approximately the same nitrate concentration but with 150 g of GAC and 80 minutes hydraulic retention time achieved complete denitrification with no nitrite concentration detected in the effluent as shown in Figure 3.21. Additionally, the two experimental runs shown in Figure 3.22 and 3.23 were carried out at a nitrate concentration of 350 mg/l, and, a much shorter hydraulic retention time of 40 minutes as compared to 80 min and 120 min employed in previous experiments. The first experimental run conducted with 150 g of GAC achieved 96.3% removal with approximately 7 mg/l nitrite in the effluent. However, in the second experiment employing 300 g of GAC, the denitrification was complete, and no nitrite was detected in the effluent. The last experiment of this series employed 150 g of GAC and 120 minutes of hydraulic retention time, and was able to achieve complete denitrification, as shown in Figure 3.24, with no nitrite detected in the effluent. The purpose of the last experiment was to compare the process performance for the actual brine vis-à-vis the synthetically prepared brine. The amount of time required for nitrate reduction in the actual brine was the same as that required for the synthetic brine.

The last experiment investigated simultaneous sulfate reduction with nitrate reduction using nitrified brine concentrate of the same characteristics as above. The experiment was conducted with 300 g GAC and influent flowrate of 10 ml/min corresponding to a hydraulic retention time of 180 minutes, and the results are presented in Figure 3.25. The initial nitrate and sulfate concentrations in the influent brine were 350 mg/l and 1300 mg/l, respectively. Nitrate removal was complete within the first 400 minutes of process operation, and neither nitrate nor nitrite was detected in the effluent. The process was run for approximately 35,000 minutes to investigate sulfate removal. A sulfate reduction of nearly 45% was achieved at the end of the run. At this point, the experiment was stopped due to excessive bacterial growth and consequent clogging of the reactor. The column walls were covered with black microbial growth, which was the indication of sulfate reduction. The peaks seen on Figure 3.25 correspond to the time when

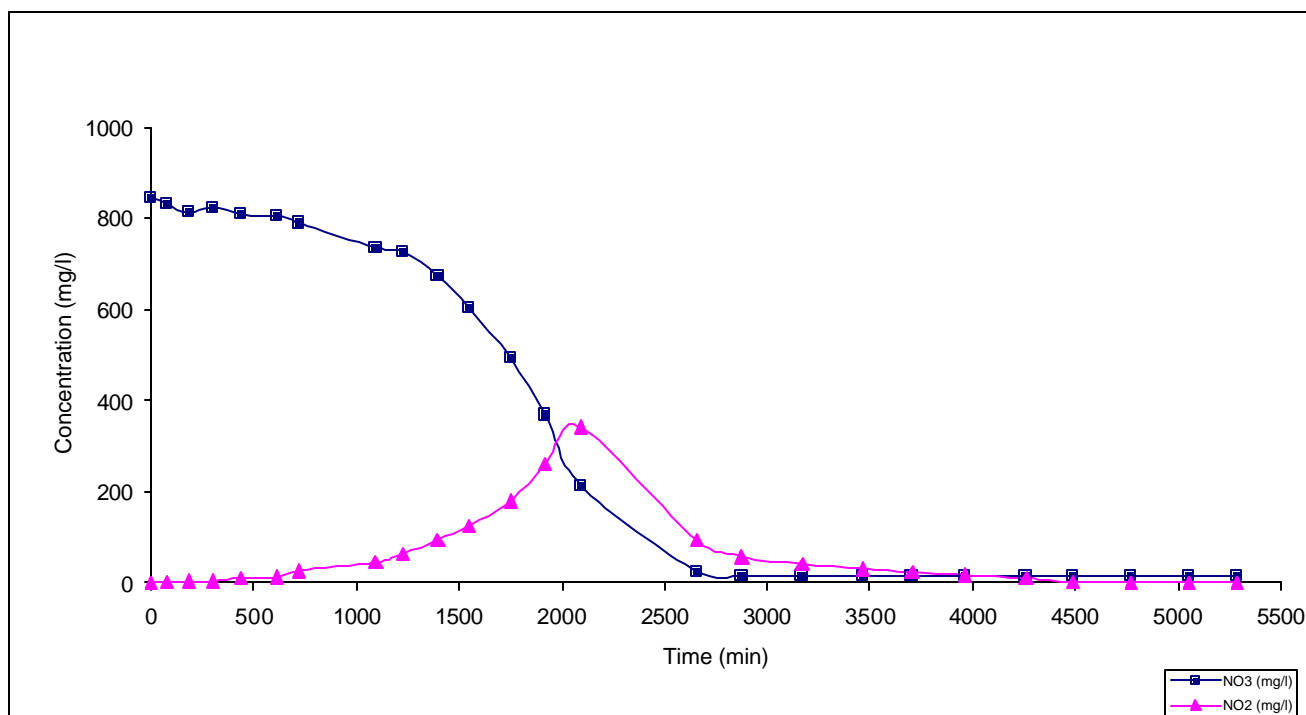


Figure 3.19. FBBR-GAC denitrification efficiency (Carbon=300 g, Flowrate=31 ml/min, HRT=56 min)

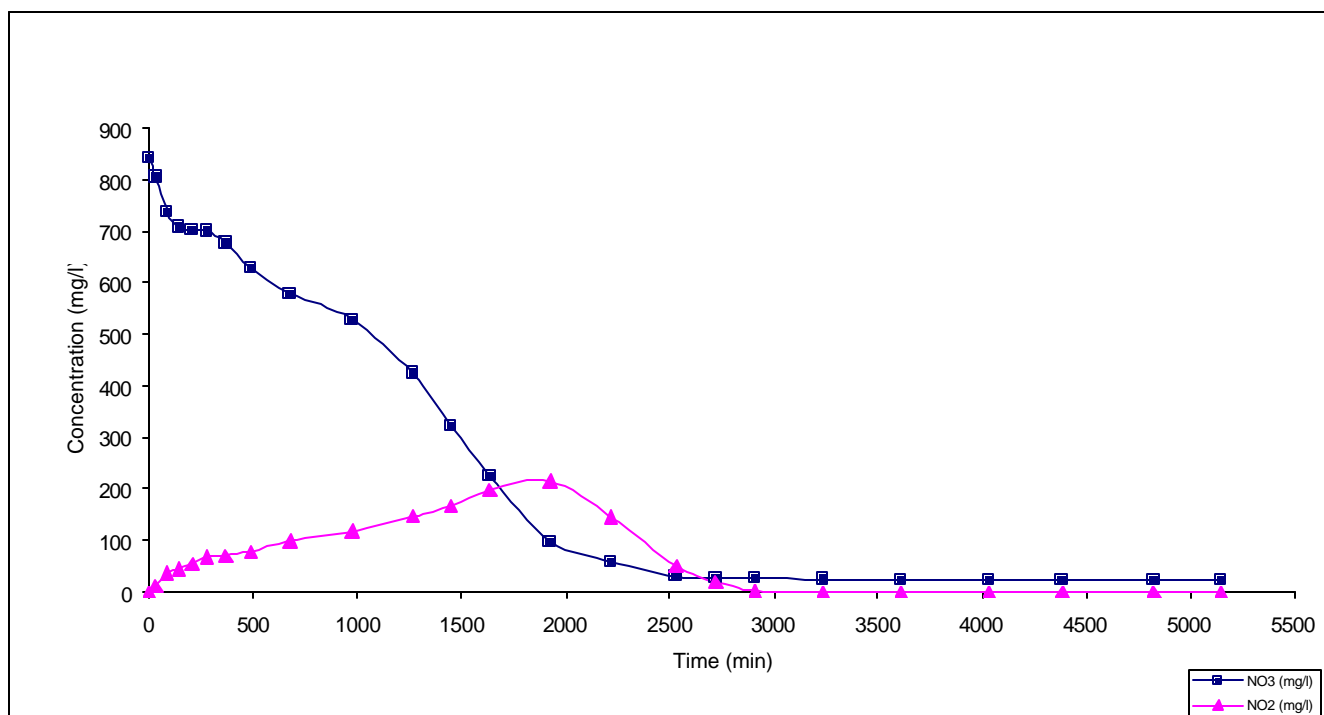


Figure 3.20. FBBR-GAC denitrification efficiency (Carbon=150 g,
Flowrate=31 ml/min, HRT=56 min)

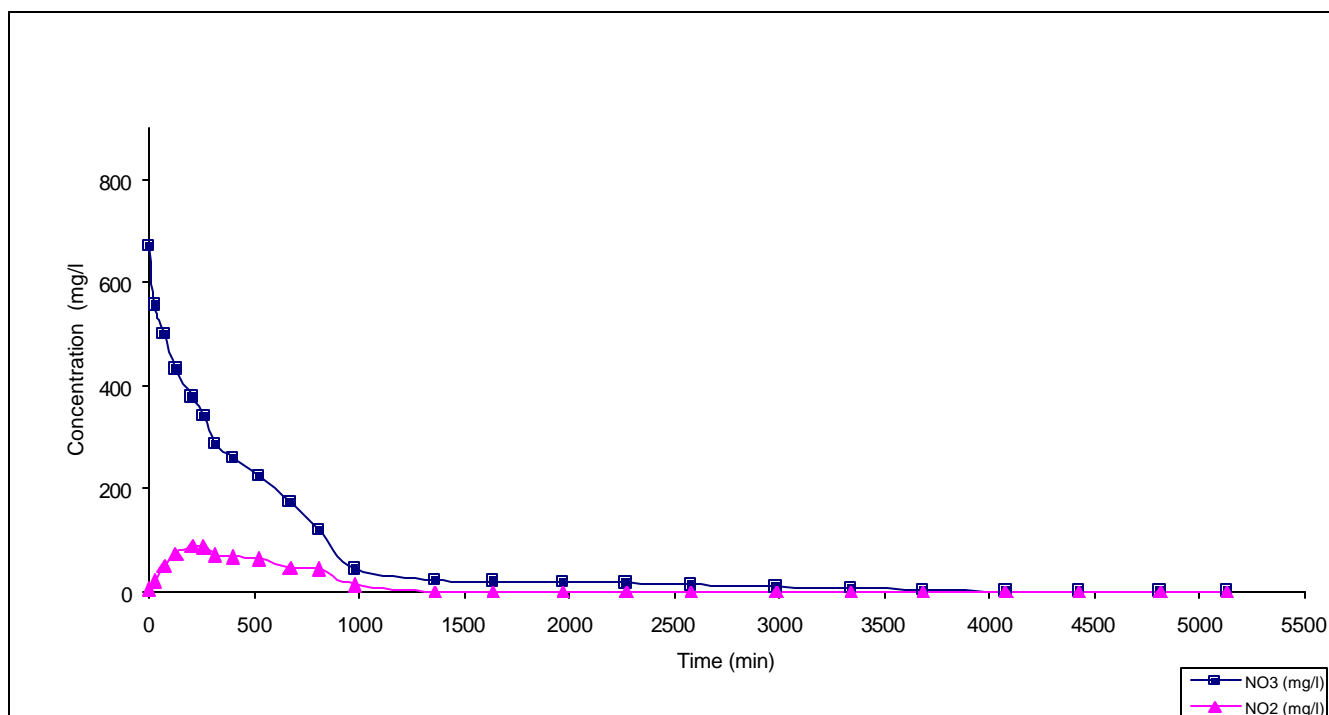


Figure 3.21. FBBR-GAC denitrification efficiency (Carbon=150 g, Flowrate=21 ml/min, HRT=82 min)

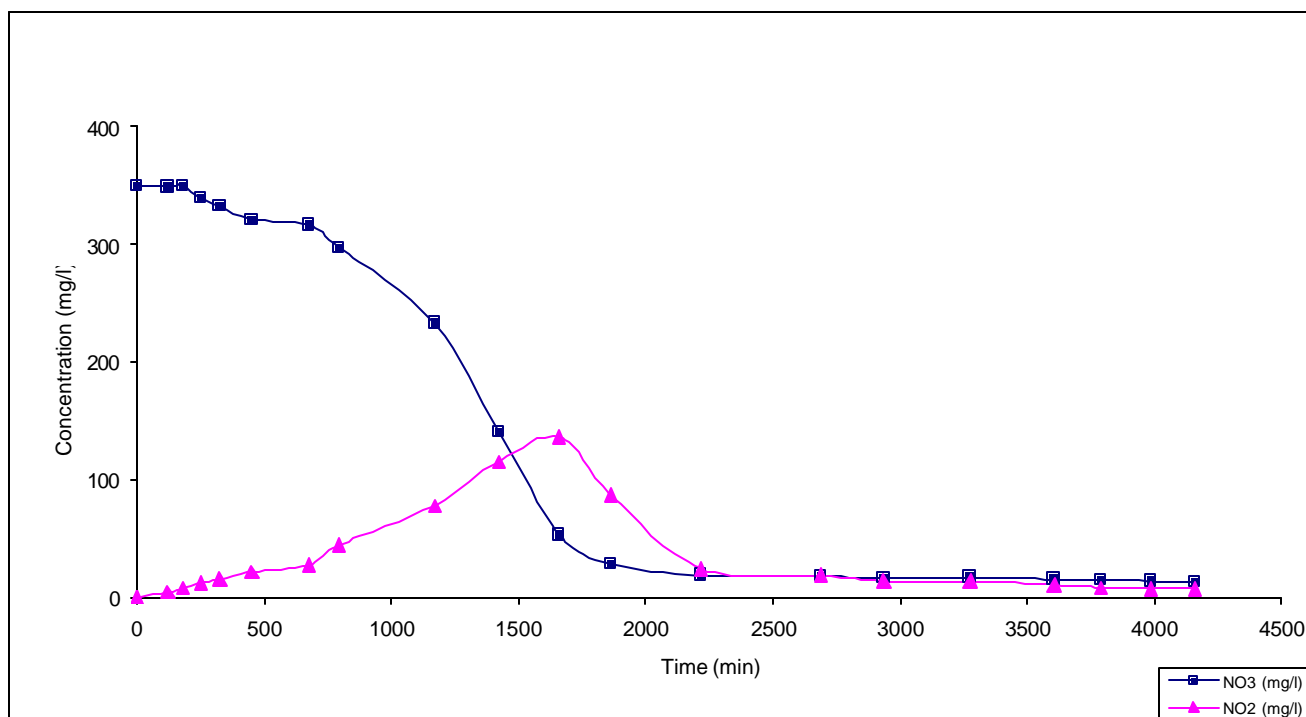


Figure 3.22. FBBR-GAC denitrification efficiency (Carbon=150 g, Flowrate=43.3 ml/min, HRT=40 min)

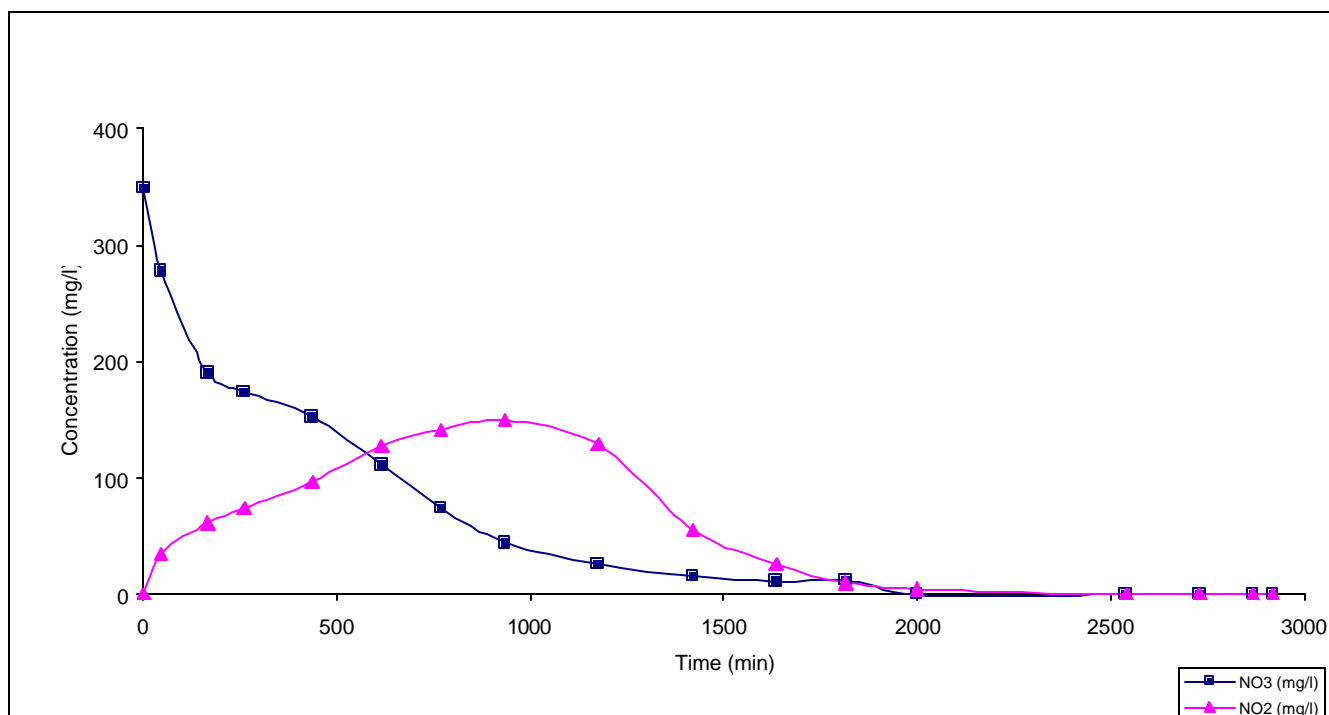


Figure 3.23. FBBR-GAC denitrification efficiency (Carbon=300 g, Flowrate=43.3 ml/min, HRT=40 min)

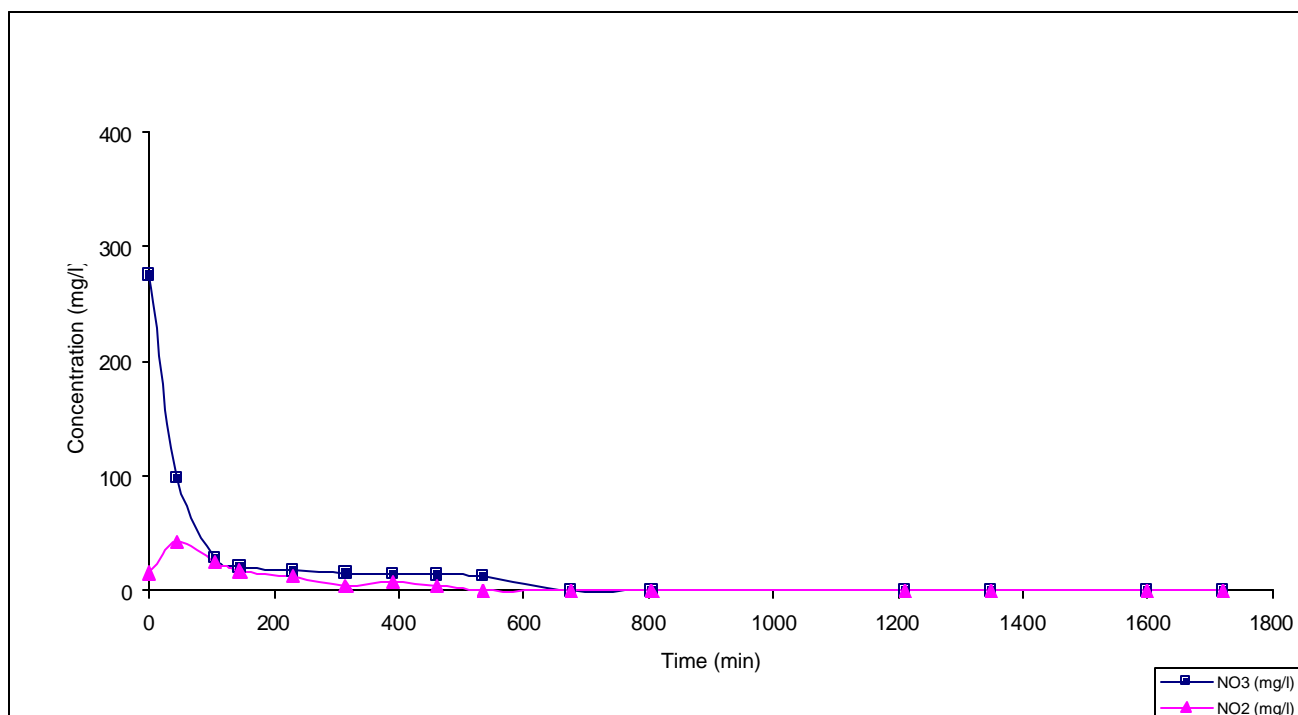


Figure 3.24. FBBR-GAC denitrification efficiency (Carbon=150 g, Flowrate=14.3 ml/min, HRT=120 min)

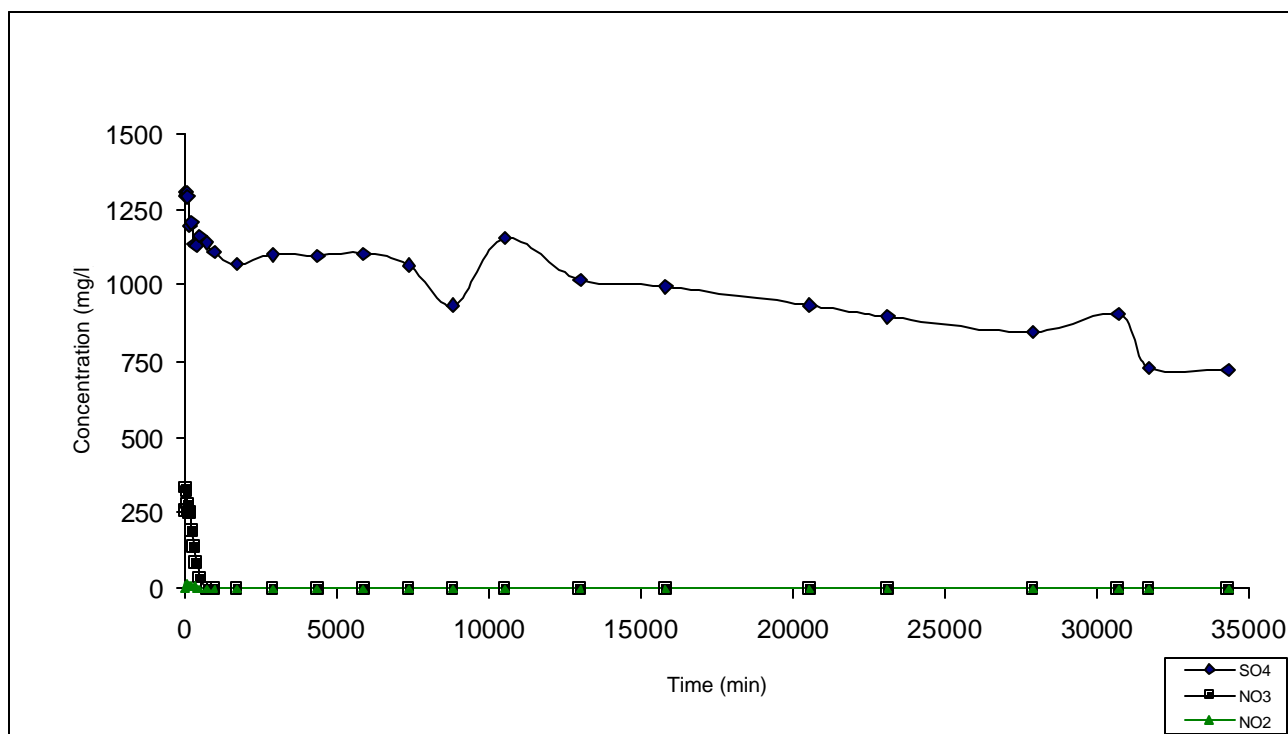


Figure 3.25. Simultaneous removal of nitrate and sulfate (Carbon=300 g, Flowrate=10 ml/min, HRT=180 min)

the GAC bed was vigorously mixed in order to remove the excess biomass growth on the particle surfaces.

3.4. Modeling of the FBBR-GAC Process

Mathematical modeling of the FBBR-GAC process was undertaken for performance prediction, designing and up-scaling of the process for denitrification of the RO brine concentrate. The modeling studies were conducted to verify the predictive capability of the model by comparing the laboratory-scale experimental data with type of the theoretical predictions, and to evaluate the dynamics of the process under different operating conditions. This is part of ongoing effort in the modeling and design of the FBBR-GAC process for denitrification applications in water treatment and water reclamation. Preliminary simulation results of the ongoing study in Figure 3.26 compares the experimental data with the predicted model profile. As evident from the figure, the model is capable of satisfactorily predicting the process dynamics from a phenomenological standpoint. Nonetheless, model refinement is underway for better accuracy in performance forecasting.

CONCLUSIONS AND RECOMMENDATIONS

4.1. Conclusions

The following conclusions are made for this part of the study:

1. The optimum temperature range for the denitrification was determined to be between 20°C and 40°C. The highest specific denitrification activity occurred at 35°C. The working temperature was chosen as 30°C for the FBBR-GAC process.
2. Although the optimum pH from the chemostat studies was determined to be 8.0, a working pH of 7.5 was chosen for the FBBR-GAC system. This was due to the fact that the pH of the nitrified effluent was around 7.5, requiring no further adjustment for all practical purposes.
3. Ethanol was chosen as the sole carbon source based on the literature review.
4. The optimum carbon to nitrogen ratio (C:N) was determined to be between 1.5 and 1.85, with the critical value being 1.5.
5. The total dissolved solid (TDS) concentration had insignificant effect on the denitrification rate.
6. Laboratory-scale FBBR-GAC studies have yielded encouraging results in terms of the denitrification efficiency and process feasibility for the treatment of RO brine concentrates. At lower detention times, the denitrification efficiency seems to be independent of the amount of GAC contained in the system. Even at higher retention times, the GAC quantity did not have any significant effect on the denitrification efficiency of the process.
7. The most significant parameter affecting the denitrification rate was the amount of biomass supported by the GAC in the column.
8. Preliminary laboratory-scale experiments revealed that the FBBR-GAC process is capable of removing approximately 45% of sulfate and 100% nitrate.
9. A predictive model was developed for performance forecasting and up-scaling of the FBBR-GAC process. The preliminary modeling simulation/prediction results are encouraging. Nonetheless, more studies are underway to upgrade the model.

4.2. Recommendations

It is recommended that the FBBR-GAC process be further investigated in laboratory scale as well as in pilot scale in order to assess its energy efficiency and cost-effectiveness. Sulfate reduction is an additional advantage of the FBBR-GAC system described above. However, more investigation is needed in order to upgrade the system for better sulfate removal. Additionally, a model may be developed for the biological removal in dual-substrate systems (in this case, nitrate and sulfate). Furthermore, detailed experimentation is needed to formulate a model that predicts simultaneous nitrate and sulfate removal in such systems.

4.3. Benefits to California

As mentioned in the introduction section, water recycling is foreseen as one of the best alternatives to meet the ever-increasing water demand. It is through recycled water that the depleted groundwaters are replenished, saline water intrusion from the ocean is prevented, and surface waters are augmented. California is one of the states that will suffer severely from polluted or depleted water resources in the near future. Currently, water demand in Southern California is being met by imported water from the northern region and from the Colorado River Project. This method of supply is highly expensive and not reliable from a long-term perspective. Therefore, the Orange County Water District, one of the leading research utilities in the US, is currently involved in extensive research on water recycling and groundwater replenishment.

Increasing population has resulted in increased water demands, which has forced the OCWD to increase its plant capacity. Since the plant is confined to a residential area, the required level of expansion is not possible. Therefore, an alternative to the existing conventional treatment plant has been investigated, which is the application of reverse osmosis technology. So far, the research on different kinds of membranes and the quality of water produced have given satisfactory results. The utility has, therefore, planned to replace its entire conventional water treatment system by the reverse osmosis unit. In the very near future, the reverse osmosis unit will be put into operation at full capacity.

The finished water quality achievable in reverse osmosis process technology is above the set standards. However, as all other processes, it has a side waste called “brine stream” categorized among hazardous materials. Almost 15% of the water recycled through the membranes is wasted as brine concentrate. The brine waste stream is extremely concentrated with

ammonia, sulfate, chloride, phosphate, and heavy metals, the constituents that render the brine concentrates hazardous waste and must be disposed of accordingly.

The current practice of handling the reverse osmosis brine concentrates is ocean disposal. However, as the utility implements the full-scale RO project, the regulatory agencies may not allow this option. As the RO membranes are established as an integral part of a new treatment system, and are currently implemented on a large scale throughout California by other water utilities, the disposal will become a problematic issue by these agencies. Moreover, further treatment may be required by the regulatory agencies. For these reasons, proper handling and disposal of brine concentrates must be planned ahead of time during the initial planning stage of the membrane processes.

The Fluidized Bed Biofilm Reactor with Granular Activated Carbon technology that has been introduced and discussed in this report, has been proven to be very effective in the treatment of the RO brine concentrates. It is capable of removing nitrates completely sulfates partly from the brine waste streams. Furthermore, it is conceivable to upgrade the FBBR-GAC system to achieve sulfate reduction. One notable advantage of fluidized bed reactors is that they require minimal space, and the reactor size is relatively smaller as compared to conventional techniques due to excessive biomass growth. The reaction time is short and the treatment efficiency is high, making it easily adoptable by the utilities planning to employ the RO technology to recycle water, in residential areas where land availability is scarce or limited.

We strongly believe that California State will benefit from the FBBR-GAC technology when the RO is widely implemented in the very near future and when the regulatory agencies adopt new regulations related to RO waste streams.

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Nomenclature

D=Dilution rate
 D_x = axial (hydrodynamic) substrate dispersion coefficient (L^2/T)
 D_f = biofilm substrate diffusion coefficient (L^2/T)
 D_s = surface substrate diffusion coefficient (L^2/T)
 k_d = endogenous decay coefficient ($1/T$)
 k_{fc} = substrate mass transfer coefficient obtained from FBBR experiments (L/T)
 K_F = Freundlich capacity constant (M/M)
 K_s = half saturation constant (M/L^3)
 L = length of FBBR (L)
 L_f = biofilm thickness at any time (L)
 L_{f0} = initial biofilm thickness (L)
 $L_{f,max}$ = maximum biofilm thickness (L)
 n = Freundlich intensity constant (dimensionless)
 q = substrate concentration in adsorbent phase (M_s/M_q)
 q_0 = adsorbent phase concentration in equilibrium with the initial fluid concentration (M/M)
 q_s = substrate concentration in adsorbent phase at the biofilm-adsorbent interface (M_s/M_q)
 Q = fluid flowrate (L^3/T)
 Q_r = recycled fluid flowrate (L^3/T)
 r = radial coordinate (L)
 R = GAC particle radius (L)
 S = bulk substrate concentration at any time (M/L^3)
 S_0 = initial substrate concentration (M/L^3)
 S_e = effluent substrate concentration (M/L^3)
 S_s = substrate concentration at biofilm-adsorbent interface (M/L^3)
 S_f = biofilm substrate concentration (M/L^3)
 $S_{f,avg}$ = average biofilm substrate concentration (M/L^3)
 $S_{f,max}$ = maximum biofilm substrate concentration (M/L^3)
 S_b = substrate concentration at bulk liquid-biofilm interface (M/L^3)
 t = time coordinate (T)
 t_{max} = time at which the bifilm thickness is maximum (T)
 v_x = interstitial fluid velocity (L/T)
 V_a = total dry volume of adsorbent (L^3)
 x = axial coordinate (L)
 X_f = biomass density (M_x/L^3)
 Y = yield coefficient (M_x/M_s)

Greek Symbols

ε = bed porosity (dimensionless)
 ρ_a = GAC density (M/L^3)
 μ_m = maximum specific substrate utilization rate ($1/T$)

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